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ORR'S

CIRCLE OF THE SCIENCES.

ELEMENTARY CHEMISTRY

OF

THE IMPONDERABLE AGENTS

AND OF

INORGANIC BODIES,

INCLUDING

LIGHT, HEAT, ELECTRICITY, AND MAGNETISM; THE SIMPLE CHEMICAL BODIES, AND THEIR INORGANIC COMPOUNDS.

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MDCCCLV.

PREFACE.

THE reader who has perused the early sheets of this volume during their course of publication in the "CIRCLE OF THE SCIENCES," will have remarked the circumstance of their anonymous character, notwithstanding that the other branches of science have appeared in the same publication with the authors' names attached. The explanation is as follows:—

In the year 1852, I was commissioned to re-edit the last edition of the late Dr. Henry's Treatise on Chemistry, published nearly thirty years since, retaining such parts of that celebrated work as might be accordant with our present state of chemical knowledge, and remodelling what had become old and out of date. With this object in view, I had nearly completed the imponderable agents, when circumstances rendered it desirable that the original intention should be abandoned, and that the sheets already prepared should appear in a serial form in the "CIRCLE OF THE SCIENCES." I readily acceded to this proposition; but the acquiescence entailed a minor difficulty, which the preface alone could satisfactorily explain. Although the portion concerning light was entirely original, and the sections on electricity and its collaterals very nearly so, I could not with any propriety call the treatise mine without incurring the charge of plagiarism; and to have denominated it a new edition of Henry's Elements, seeing the extensive alterations which had been made, would scarcely have been more appropriate; hence, in the opinion of all concerned, the decision of allowing the sheets to appear anonymously was thought desirable. Mature consideration of the facts of the case have satisfied me that the course adopted was, under the circumstances, preferable to any other.

The merits of Dr. Henry as a chemist are especially recogniz-

able in his investigations on gases; and by a peculiarity in the arrangement of his work, the general philosophy of gases is described under the head of heat. Now, it so happens that this portion of chemical science has undergone, subsequently to the time of Dr. Henry, a less amount of fundamental change than any other;—the investigations of chemists since that time, relative to this portion of science, having been merely the amplification of what he so successfully began: hence the retention of this portion of his treatise would have enhanced the value of any chemical book whatever. I regard it, therefore, advantageous to the interests of the present publication that circumstances have enabled me to preserve it almost intact.

As regards the second portion of the volume, or that relating to the chemical elements and their inorganic combinations, I am wholly responsible; and I trust that—although the space at my disposal has been circumscribed—no considerable matter of interest or importance will have been omitted.

Produced in the serial form, hurriedly and at intervals, as this volume has been, some inaccuracies have necessarily crept in; yet not of greater importance, or in greater number, I am disposed to believe, than may be usually discovered in first editions of scientific works. Those already noticed will be seen in an appended slip of *errata* and *corrigenda*.

J. SCOFFERN, M.B., LOND.

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ERRATA ET CORRIGENDA.

Page 4, line 12, *for* above *read* below.—And, as an illustration to the paragraph, conceive the balance-beam to be inverted. The woodcut is an actual copy of the beam of a very delicate balance, without the pans. When the latter are attached the centre of gravity will be brought lower down, as is obvious.

4, line 24, *after the words* a thousandth part *insert* of a grain.

306, line 17 of text, omitting diagrams, *for* peroxide of barium *read* peroxide of hydrogen.

349, line 3 from the bottom, *for* now discover *read* soon discover.

371, line 3, insert 32 for the equivalent number of phosphorus.

The Subscribers to the CIRCLE OF THE SCIENCES are respectfully informed that a Volume on PRACTICAL CHEMISTRY will be immediately commenced, an early number of which will contain PHOTOGRAPHY, by Mr. Sparling, assistant to Mr. Fenton; and ELECTRO-METALLURGY, by George Gore, Esq., Birmingham.

DALTON. DAVY. LAVOISIER.

THE ELEMENTS OF CHEMISTRY.

Definition of Chemistry.—Chemistry is the science which investigates the quality and constitution of matter in all its relations, except those affecting visible motion and space. Its agencies involve all the grand forces of the universe except gravitation; which latter belongs to the department of mechanical philosophy. Even the force of gravitation, however, comes indirectly under the chemist's scope, as affecting the weight and the specific gravity of ponderable bodies. Its peculiarities, therefore, as contra-distinguished from those of the other forces, will have to be discussed.

All bodies, composing the material system of the universe, have a natural tendency to approach each other, whatsoever may be the distances at which they are placed. The operation of this force extends to the remotest parts of the sidereal system, and is one of the causes which preserve the stability of planets and comets in their orbits. The smaller bodies, also, that are under our more immediate observation, are influenced by the same power, and fall to the earth's surface, when not prevented by the interference of other forces. From these facts, the existence of a property has been inferred, which has been called *attraction*, or, more specifically, the *attraction of gravitation*. Its nature is entirely unknown to us; but some of its laws have been investigated, and successfully applied to the explanation of phenomena. Of these laws, the most important are, that the force of gravity acts on bodies directly in proportion to the quantity of matter in each; and that it decreases in the reciprocal proportion of the squares of the distances.

From viewing bodies in the aggregate, we may next proceed to contemplate them as composed of minute particles. These particles, it is probable, consist of solids, which are incapable of mechanical division, but are still possessed of the qualities of

length, breadth, and thickness. In simple bodies the particles must necessarily be all of the same nature, or *homogeneous*. In compound bodies, we are to understand, by the term *particles*, the smallest parts into which bodies can be resolved without decomposition. The word *atom* has of late been revived, to denote both these kinds of particles; and we may therefore speak with propriety of *simple atoms* and of *compound atoms*. When two atoms of different kinds unite to form a third or compound atom, we may term the two first, *component atoms*; and, if these have not been decomposed, they may be called *elementary* or *primary atoms*.

The atoms or particles of bodies are also influenced by the force of attraction, but not unless when placed in *apparent* contact. Hence a distinction has been made between gravitation, and that kind of attraction which is effective only at insensible distances. The latter has been called *contiguous attraction*; and it has been furthermore subdivided as exerted between particles of matter of the *same* kind, or between particles of a *different* kind.

Attraction of Aggregation.—Cohesive attraction, or more simply cohesion, is to be understood that force or power by which particles or atoms of matter *of the same kind* attract each other; the only effect of this attraction being an aggregate or mass. Thus a lump of copper may be considered as composed of an infinite number of minute particles or integrant parts, each of which has precisely the same properties as those that belong to the whole mass. These are united by the force of cohesion. But if the copper be combined with another metal (such as zinc), we obtain a compound (brass), the constituent parts of which, copper and zinc, are combined by the power of *chemical attraction or affinity*; a term which it is proper to restrict to the attraction existing between particles of *different* kinds. In simple bodies, therefore, cohesion is the only force exerted between their particles. But in compound bodies we may distinguish the force, with which the *primary* or *component* atoms are united, from that which the *compound* atoms exert towards each other; the former being united by chemical attraction or affinity, and the latter by cohesive attraction.

Hence we deduce a well-defined and easily appreciable distinction between the three forces or attractions of gravitation, cohesion, and chemical attraction, or affinity. Gravitation operates between masses of matter, of whatever kind, and at sensible, frequently enormous distances. Cohesion operates between particles, *not masses*, and of similar kind, at distances which are inappreciable. Chemical affinity, or attraction, operates between particles, *not masses*, of dissimilar kind, and also at inappreciable distances. As illustrations of the propriety of the definitions assigned to these three forces, a few simple examples may be given. First, with respect to gravitation, it may be remarked that any ponderable substance, of whatever kind—for example, a stone, a lump of metal, or a piece of wood—if allowed perfect freedom to move, falls towards the earth; thus proving, that although a stone, a piece of metal, and wood, are all masses of different kind, yet they are affected by a certain force, exerted mutually between themselves and the earth, at distances which can be measured, and which are therefore sensible. That which has been demonstrated as holding good of three masses of different kind, may be proved to hold good for all ponderable bodies whatever. Hence the universality of the law.

The reader who is just commencing his studies in physics and chemistry, may probably meet with some examples which are seemingly at variance with the law here enunciated as universal. Thus hydrogen gas possesses weight; yet a balloon filled with this gas does not fall towards the earth, but rises. The apparent discrepancy

between the phenomenon observed, and the enunciated law, consists in this—namely, the presence and the concomitant influence of atmospheric air; which, being heavier than hydrogen, sinks beneath the balloon containing the latter, and lifts it up.

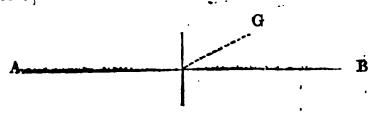
To illustrate the peculiar nature of the attraction or force of cohesion, we may assume a mass of metal to be the subject of observation. By the application of sufficient force this mass may be dissevered into smaller parts, and no amount of pressure can force them so closely together that they shall unite. Hence cohesion, the attraction which held the particles of metal together, and made them constitute one mass, acts at insensible distances. It is evident, moreover, that the attraction is exerted between particles of similar kinds.

To illustrate the propriety of the definition given to chemical attraction or affinity, the example of blue vitriol may be cited. This substance is a mass made up of particles, as may be demonstrated by grinding it to powder. But if the smallest appreciable particle of this powder be taken and examined, it will be found to be composed of sulphur, oxygen, and copper, united together by some force acting at an insensible distance, but exerted between dissimilar particles.

The Operation of Weighing.—All terrestrial substances are attracted, as we have seen, towards the earth's centre, by the force of gravitation in direct proportion to their *mass*, or the quantity of matter which they contain; and the estimation of this mass constitutes the process of weighing, so indispensable in all accurate chemical investigations. Hence the scales or balance become to the chemist what the rule and compasses are to the mathematician—the starting point of all his investigations—the measure of their correctness.

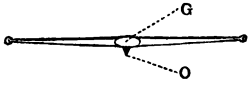
The general functions of a pair of scales are so universally known, that their minute description may be thought unnecessary. The chemical student, however, will do well to make himself acquainted with certain points in relation to these instruments—their varieties, their principle of construction, and the theory of their action—some of which points are not very obvious from a casual inspection. As to their varieties, it may be mentioned that the less delicate instruments of this kind are simply termed *scales*, and are employed for operations of weighing, when moderate accuracy alone is required; the term balance being restricted to those delicate instruments so indispensable to the prosecution of accurate experiments, but which are unfitted for common use. In principle, however, the *scales* are identical with the *balance*,—a designation which I shall hereafter employ in a generic sense.

The balance, as generally defined, may be considered as an uniform inflexible lever, supported horizontally at the centre of gravity, and supporting weights, at equal distances from the centre, by points in the same horizontal line with the centre of gravity. Such is the balance theoretically considered; but in practice there is a considerable deviation, partly because of the impossibility of securing all these conditions on account of mechanical difficulties, and partly on account of deviations specially introduced, for reasons to be described hereafter.



For the purpose of entering upon a consideration of the theory of the balance, let us assume G to indicate the centre of gravity in the beam A B; by which is meant that point on which, if the beam were poised, it would remain in perfect quietude. Supposing now a weight to be attached to either of the extremities, A or B, it is evident that the extremity so weighted would fall, and

that the original horizontal position of the beam could only be maintained by adding to the second extremity a weight equal to that previously added to the first. Practically speaking, however, a balance such as here described, in which the extremities are supposed to be on the same horizontal line with the centre of gravity, is inefficient. An instrument of this kind turns with the minimum of added weight, it is true, and in this sense possesses the extreme of delicacy; but when turned, it no longer recovers its position by vibration, preparatory to assuming its final condition of rest, as a good balance should do, but assumes a condition of rest at once. This is technically called setting. Hence practice indicates that an efficient balance should not have its centre of gravity exactly coincident with its centre of oscillation, but more or less above it, according to the amount of weight the balance is designed to carry. This deviation is indicated by the accompanying diagram, where G, as before, represents the centre of gravity, and O the centre of oscillation. Hence it may be remembered, that in proportion as the quantity intended to be weighed is small, so ought the centre of oscillation to be nearer the centre of gravity, or *vice versâ*.



The greater number of modern balances are furnished with the means of varying the position of the centre of gravity at pleasure, by the elevation or depression of a screw weight, situated either above or below the beam. Balances used for the mere purposes of mineral assaying need not be adapted to the carrying of larger amounts of weight than thirty grains in each pan; but a delicate balance for general chemical analysis must at least be capable of sustaining a weight of one thousand grains in each pan, and, if good, should turn when thus loaded with a thousandth part. Before employing a balance, care should be taken that it stands quite evenly on the table. This is easily seen by means of two spirit levels attached to the base plane of the instrument case, or by a plumb line. The adjustment may then be readily effected by means of screws regulating the elevation of each corner of the frame, or case, in which the balance is contained.

Substances to be weighed should be rarely, if ever, put into the naked pan of the balance, but inclosed in a tube or capsule; nor should they be, under any circumstances, introduced whilst hotter than the surrounding air. Under these circumstances there would be developed an ascending current of air, causing the body to appear lighter than reality; which would of course vitiate the result.

Every care should be taken, by keeping the instrument dry, to prevent rust or corrosion; but if by chance a spot should be rusted or corroded, so as to destroy the equilibrium of the beam, never under any circumstances attempt to remedy the defect by filing, scraping, or scouring. For the time being, accomplish equilibrium by means of a counterpoise; and, when convenient, let the philosophical instrument-maker do the rest.

All delicate balances have their points of oscillation composed of a steel knife-edge working on agate planes. These knife-edges are subject to be damaged by sudden concussions; hence the impropriety of putting anything into either scale whilst the beam is in motion. It should therefore be brought invariably to rest, and the weights added or subtracted whilst in this state.

Although a hundredth is usually the smallest submultiple of the given amount employed in practice, delicate balances, such as described, are always preserved in glass cases, for the purpose of protecting them against dust and moisture. They

cannot be retained without damage in the laboratory, but should be kept in a dry room, and a basin of quicklime should be placed within their case for the purpose of absorbing acid fumes and moisture. In addition to the delicate balance, scales and weights are required for ordinary operations; but any special description of these is unnecessary.

It remains to be stated that the upward pressure of atmospheric air against a falling body (*i. e.*, in the case under consideration, the body weighed) is not usually taken cognizance of in conducting the operation of *absolute* weighing, as distinguished from relative weighing (*i. e.*, taking specific gravities). In the latter case, however, when extreme delicacy is required, this upward pressure must be accounted for.

Taking Specific Gravities.—As the weight of a body is the numeral expression of its gravitating force, so the specific weight, or specific gravity, of a body is the numeral expression of its gravitating force in relation to an equal measure of some other body fixed upon as a convenient unity of comparison. Thus if we consider the weight of a given bulk of water, for example, to represent unity, we may state that the weight of an equal bulk of copper, or lead, or mercury is greater than that of water in the ratio of 8·667, 11·381, and 13·545, which numbers are said to represent the specific gravity of these metals—water being the accepted standard of comparison for all solids and liquids. Again, if we assume the weight of a given bulk of atmospheric air to represent unity, we may state that the weight of an equal bulk of any gas or vapour is so much greater or less than that bulk of air, which expressions will be indicative of the specific gravity, or specific weight, of such gases or vapours—air being accepted as the standard or unity of specific gravity for this class of substances.

The reason why water has been accepted as the standard of specific gravity for solids and liquids, and atmospheric air for gases and vapours, is purely one of convenience. Any other standard might have been selected without theoretically affecting the result.

Such being the explanation of what is meant by the term specific weight or specific gravity, the theoretical means of arriving at the desired result are obvious; nothing more being necessary than to select equal bulks of substances to be operated upon, to weigh them, and to ascertain the ratio between their respective weights. Thus, for instance, a cubic inch of water, accurately measured at the temperature of 60° F., would be found to weigh 252·458 grains, and a cubic inch of the metal copper 3157·44 grains, thus presenting the ratio of 1 to 8·667 grains.

In practice, however, this mode of taking specific gravities is rendered impossible by many impediments. Not only is it impossible to measure out equal bulks of any substances, but in many cases it would be impossible to reduce the substance, of which the specific gravity was desired, to any defined mathematical shape, so as to adapt it to the process of direct measurement. Thus, for instance, the case often presents itself where the specific gravity is required of an irregularly-shaped specimen of metallic ore, the integrity of which must not be destroyed; here the process of attempting to reduce it to the form of a cube could not be entertained. Again, the material might be in the condition of sand, to which the theoretic indications of taking its specific gravity by direct measurement would be equally inapplicable. Hence certain indirect methods of arriving at the desired result must be devised.

In describing these indirect methods I will first assume the case of an irregular solid mass, of which the specific gravity is desired. The first point to be determined is the weight of its own bulk of water, which should seem obtainable by immersing it

in a vessel quite full of that liquid, and accurately collecting all that portion of water which might be displaced. Practically, however, this is impossible; for not only would a portion of the liquid thus circumstanced adhere round the sides of the vessel, but another portion would evaporate; to say nothing of the occurrence of the well-known phenomenon witnessed in pouring a liquid into a dry glass, characterized by the rise of the liquid considerably above the level of the vessel. Hence some more indirect method of obtaining the weight of a bulk of water, equal to that of the substance operated upon, must be devised; and the following consideration renders the obtaining of this function most easy. Any substance will, if immersed in water, be pressed up with a certain force equal to the weight of its own bulk of water. Hence, if the substance to be immersed be made to depend from one extremity of the beam of an equipoised balance, it is evident that, on account of the upward pressure of the water, a temporary loss of weight of the substance immersed will be sustained; and this loss of weight, being equal to the weight of its own bulk of water, may be readily determined by adding, to the opposite scale-pan, such an amount of weight as will suffice to bring the beam once more into equilibrium. Hence the practical rule to be followed, in taking the specific gravity of substances by the method indicated, may be succinctly said to consist in weighing the substance to be examined, first in air, then in water and, finally, dividing its weight in air by its loss in water.

Reducing these directions to a formula, let the specific gravity of a body be represented by G, its weight in air by w, its weight when immersed in water by $w - x$;

$$\text{Then } G = \frac{w}{w - x}.$$

After what has been said on the variation effected by atmospheric air on the apparent weight of bodies, it will be easily inferred, that when extreme delicacy is required, the weight of the bulk of air, equal in size to the bulk of substance operated upon, must be taken into consideration. If, therefore, we indicate this element of calculation by u, the formula will be thus modified:— G = specific gravity, w = weight in air, $w - x$ = weight in water, u = weight of air equal in bulk to that of the substance operated upon;

$$\text{Then } G = \frac{w + u}{w + u - x}.$$

The modification of scale-beams, by which specific gravities are taken as indicated, consists of a pan suspended by shorter wires or strings than those employed for common purposes, and supplied with a hook inferiorly attached to which, by a hair or filament, the substance under examination is intended to be hung. The suspending filament should be, by preference, unspun silk or human hair; but horse-hair is frequently used, and answers sufficiently well when the substance under consideration is large, and extreme accuracy in not required.

The hair, or other filament, employed as a means of suspension between the pan of the balance and the substance to be weighed, may either be attached to the latter directly or indirectly: if indirectly, a double metallic hook, as represented in the accompanying diagram, is employed; and its apparent weight in water must be taken into account in calculating the result. For this purpose the apparent weight in water of the mineral and hook being noted, the mineral should be removed; and weights being now added to the suspending pan, until the re-establishment of an equipoise, the amount of weight thus added will be equal to the apparent weight of the hook in water.

The water employed is always understood to be distilled water, at a temperature of 60° F.; but rain water, or even spring or river water, may be employed in some cases. No considerable deviation, however, from the temperature of 60° F. should be permitted, as in that case the errors arising would be serious; and care should be taken that no air-bubbles, which may accidentally attach themselves to the substance under examination on to the suspending filament, remain whilst the counterpoise is being effected. With distilled water, or water that has been boiled, no such bubbles will occur; but with common water they are almost invariably present, and should be carefully removed by means of a camel's-hair pencil.

There are certain cases in which water cannot be thus directly employed because of the solubility in that fluid of the substance to be examined. This remark, for example, would apply to a mass of sugar or of soap, both of which are readily soluble in water. The specific gravity of such bodies may be determined by employing certain fluids of known specific gravity, and in which they are insoluble. Thus pure alcohol might be employed in the case of sugar, and a saturated solution of salt and water in the case of soap.

Another case involves the taking of the specific gravity of a substance lighter than water; under which circumstances it will not sink, and a modification of the process described must be had recourse to. The weight of the lighter body in air having been determined, and of the heavier body in water, both are to be fastened together, and weighed in water, when their aggregate weight will fall short of that of the heavier body. The weight of the lighter body is now to be subtracted from that of the heavier body, and the remainder added to the weight of the former in air. The quotient indicates the weight of a quantity of water equal in bulk to the lighter body. The weight of the lighter body in air being now divided by the latter sum, its specific gravity is deduced.

The heavier body thus employed may be the supporting hook itself, made for this purpose of adequate weight, and sufficiently large to admit of being bent around the substance to be immersed. Supposing the weight of atmospheric air to be omitted, the formula in this case will be

$$G = \frac{w}{w + x}.$$

Or u being the weight of air displaced by the mineral,

$$G = \frac{w + u}{w + u + x}.$$

The method of taking the specific gravity of disintegrated particles is different from that already described, although in principle it is identical; the object being in either case to determine, as a preliminary, the weight of an equal bulk of water. It consists in taking a bottle of such a size as to contain a known weight of water—say 1,000 or 500 grains. Such a bottle being accurately filled with water, a given weight of the powder to be examined is dropped in; when it follows that an amount of water equal in weight to that of the bulk of substance under examination must overflow, and which, although it cannot be collected and weighed, for reasons already described, may be readily estimated by the loss; thus furnishing the usual elements of calculation for specific gravities.

Another means of estimating the specific gravity of powders and comminuted

particles generally consists in weighing them in a small cup, or crucible, as hereafter represented.

Here the cup or other vessel performs the function of the double hook, and must be allowed for in a similar manner.

The process for obtaining the specific gravity of liquids is as follows:—A bottle of such a size as to contain a known weight of water is filled with the liquid to be examined and weighed. In proportion as the result is greater or less than the weight of water, so is the liquid under examination of greater or lesser specific gravity.

Let x = the weight of the bottle filled with the liquid, and stoppered; y the weight of the bottle filled with water, and stoppered; u the weight of the bottle empty (*i. e.* filled with atmospheric air), and stoppered,

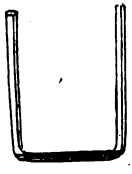
$$\text{then } G = \frac{x - w}{y - w}.$$

Or supposing the weight of air contained within the cup to be estimated,

$$\text{then } G = \frac{x + u - w}{y + u - w}.$$

In order to save trouble, bottles are sold so adjusted that they contain a known weight of water at 60° F., usually 500 or 1000 grains, and supplied with counterpoise or tare for the bottle or stopper. These instruments are purchased under the name of *five hundred grain* or *thousand grain bottles*, and are obviously calculated to save time, inasmuch as only one process of weighing has to be performed, and the specific gravity of a substance operated upon is read off at once without any calculation. These bottles, however, are seldom correct; moreover, it frequently happens, in the course of chemical operations, that the specific gravity is required of liquids of which the operator possesses much less than 500 grains; and when mere saving of time, at the expense of accuracy, is the object aimed at, this can be still better accomplished by employing the hydrometer.

Ordinarily, the best instrument for taking the specific gravity of liquids consists in a segment of glass tube, closed at one end, and ground at the other. Probably the most convenient size for general purposes is that represented by the accompanying woodcut.



Grinding the open end may be accomplished by a common file used wet, and the cover may be a circular disc of very thin wood or glass. Special instructions for the manufacture of small glass instruments will be hereafter given. It may be as well, however, in this place to indicate that a thin piece of sheet glass may be cut, with tolerable facility, *under water or other liquid*, by means of a common pair of scissors; the contact of liquid preventing the spread of those irregular vibrations to which fractures are attributable. Having in this way cut out a disc of the size required, its edges should be trimmed by means of a wet file; and being numbered or marked, its weight should be taken, and recorded in the laboratory book for reference.

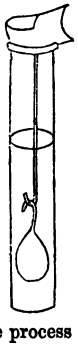
In whatever pieces of glass apparatus, subject to the operation of weighing, ground edges occur, care should be taken to have the grain so fine that no chips are likely to be removed; otherwise the weights indicated for each would be liable to continued variation.

The operation of scratching on glass may be conducted either with a variety of diamond, known as the *scratch diamond*, sold by this name on purpose; or, what is just as effectual, the angular extremity of a newly-broken file. Sometimes, instead of a conventional mark inscribed on a piece of glass before weighing, the actual weight, of course written *after* weighing, is inscribed; this, however, is a bad plan, inasmuch as the abrasion thus accomplished necessarily vitiates the weight. Supposing a disc of glass, having the area of the diagram below, to have the quantity (gr. 10·59) inscribed on it, the abraded glass thus removed would scarcely amount to less than the two-hundredth part of a grain—an error more than sufficient to vitiate the result practically.

It remains to append yet a few other remarks on the subject of taking specific gravities by these little cups. The liquid having been poured in at the proper temperature, rather above the level of the edge, the glass disc or cover is to be put on with a sliding motion, so as to exclude every bubble of air. This operation will necessarily cause a portion of the liquid to overflow and stick about the sides, from which it should be removed by the continuous use of blotting-paper; and the cup should on no account be subjected to prolonged contact of the naked hand, which would have the effect of causing the liquid to expand and overflow. The cup must either be steadied during wiping by means of a paper loop, or else by the finger, protected either by gloves or intervening cloth from immediate contact with the glass.

Occasionally still more delicate means must be had recourse to for taking the specific gravity of liquids. The liquid to be examined may be so exceedingly volatile, or so small in quantity, that the mere act of pouring it into a cup would be attended with such a loss as would prevent the cover fitting with accuracy. Under these circumstances the following plan may be had recourse to:—

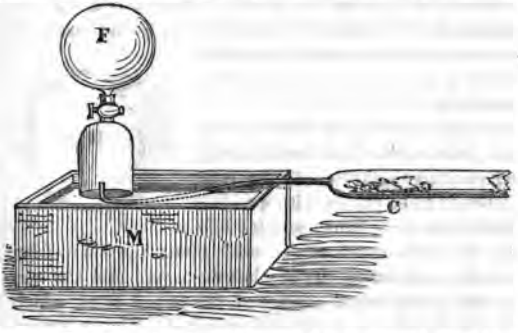
Construct, out of a glass tube, a small bulb with a tubular capillary opening, and when cold weigh it. Next wind a small piece of platinum wire loosely round the hooked part of the neck, thus: and plunge the bulb into the liquid to be operated upon in a tube, thus: Cover the mouth of the tube now with the thumb tightly; and applying the flame of a spirit-lamp to the tube containing the liquid, the air within the bulb will expand and emerge. Now, on allowing the contents to cool, the liquid will rush in through the capillary orifice, and partly fill the bulb. By one operation, however, the bulb can never be completely filled. The heating must be several times repeated to accomplish this. When the bulb is filled, the tube should be first allowed to cool to the temperature of the surrounding air. It should then be immersed in water at 60°; and, finally (the bulb being removed, and dried, if necessary, by means of blotting-paper), it should be weighed.



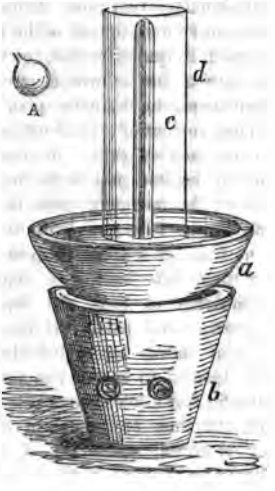
The unit of specific gravity for gases and vapours is, as I have already observed, not water, but atmospheric air; and, although the process of taking the specific gravity in this case presents some practical difficulties, its theory is very simple, being, in point of fact, precisely analogous to the theory of taking the specific gravity of fluids. A flask, or bottle, having been weighed when full of atmospheric air, the vessel is exhausted by means of the air-pump, filled with the gas or vapour to be investigated and weighed

again. In direct proportion as its contents are lighter or heavier than before, so is the substance under examination lighter or heavier than an equal bulk of atmospheric air. The numeral expression of this difference is its specific gravity.

All that has been said, as to the necessity of avoiding naked contact of the hand with vessels containing liquid under process of having their specific gravity taken, applies with still greater force to such easily expansible bodies as gases. Moreover, care should be taken that the gases under examination have been perfectly dried. This is accomplished by causing them to traverse a tube filled with pieces of dry chloride of calcium. The subjoined diagram represents a tube of chloride of calcium (C), a mercury trough (M), and a flask previously exhausted by means of the air-pump (F).

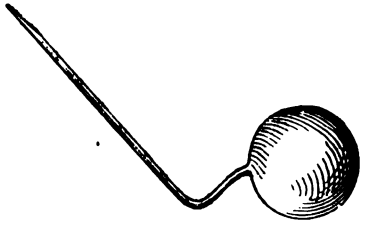


The operation of taking the specific gravity of vapours or forms of matter which retain their elastic gaseous state only within certain ranges of temperature, requires another mode of procedure. Two processes have been devised for effecting this: one by M. Gay Lussac, and the other by M. Dumas. The process of M. Gay Lussac is as follows:—A small bulb of glass (drawn here on a magnified scale, A), terminating in a small capillary jet, is filled with the liquid substance, whose vapour is to be examined. The orifice of the jet is fused by means of the blow-pipe flame, the bulb wiped dry, and placed aside for present use. A dish of mercury (*a*) is now taken; a graduated tube (*c*), also full of mercury, inverted over it, as in a pneumatic trough; and the dish, along with its tube, set to heat over a small furnace (*b*). The bulb just treated of is now thrust under the mouth of the tube, without raising the latter from the mercury; when it is evident the bulb will rise through the column of mercury, until stopped by the closed end of the tube. Matters being thus far arranged, a cylindrical glass (*d*), open at both ends, is passed over the graduated tube, and lowered until one end touches the surface of the mercury in the tube, and thus becomes a vessel of capacity, into which some colourless oil is poured, until the inclosed graduated tube is completely covered. The furnace heat being now gradually raised, the mercury becomes hot; communicating its heat to the liquid contents of the little bulb, which form vapour, press outwards, burst the bulb, depress the mercury, and pervade the tube to



the extent of vapour formed. This extent can be read off through the oil, and expresses the cubic contents of the vapour, corresponding with the temperature of the oil and the mercury at the time of the operation; which temperature is taken cognizance of by a thermometer. It is evident that the operation just described furnishes us with all the elements for learning the specific gravity of a vapour at the temperature at which the operation may have been conducted; and its specific gravity at other temperatures may be deduced by means of a calculus, to be explained hereafter. This process answers quite well for taking the specific gravity of many vapours; but it is inapplicable to those whose existence depends on such an amount of heat as would cause the decomposition and blackening of the surrounding oil.

The process of M. Dumas is applicable to all vapours whose temperature does not exceed that of melted glass, and is thus conducted:—Into a bulb of glass, with a long capillary jet, as in the diagram, is put a small portion of the substance to be vaporized; and the bulb being completely immersed, by means of a contrivance represented in the diagram, in a metal bath of tin, lead, and bismuth, the latter is heated, until the contained substance rises in vapour, and all the excess of it over and above the amount necessary to fill the bulb escapes through the capillary jet.



This point may be known to be arrived at when a current of vapour is no longer given off; and being observed, the end of the capillary jet is sealed, the bulb removed from the metal bath, cleaned, and when cold accurately weighed. Supposing the operation described to have been accurately conducted, the whole bulb will, if the end of its capillary jet be broken off under mercury, become filled with that metal. Accordingly this is the next step of the operation:—The bulb thus filled with mercury, and, with the broken-off end, being placed cold in the balance-pan, are also weighed. Finally, the mercury is removed, weighed alone, and now we have the whole data necessary for calculating the specific gravity of the vapour, as will presently be recognised.

1. By weighing we learn the weight of bulb and its vaporous contents.
2. By weighing we learn the weight of the bulb filled with mercury.
3. By weighing we also learn the weight of the mercury, whence its volume may be accurately deduced, inasmuch as one cubic inch of mercury weighs 3425·35 grains.

But the total weight of bulb and mercury, minus the weight of mercury, is equal to the weight of the bulb alone; and the weight of vapour first included is equal to the weight of the bulb, plus vapour minus the weight of bulb. Moreover the weight of mercury contained being known, and hence its bulk, the weight of atmospheric air equal to that bulk of mercury, may be deduced by calculation.

In addition to the methods of taking specific gravities already described, there exist others which, although not so correct, are occasionally more convenient, and thus better adapted to the ordinary requisitions of commercial and manufacturing chemistry.

Of these instruments the one most usually employed is that which, in a generic sense, is termed the hydrometer, a term which means the measurer (specific gravity understood) of water. This instrument, however, has various names, accordingly as it may be graduated for alcoholic liquors, when the specific term alcoholimeter is

applied; for milk, when it is called a lactometer; for sugar, when it is called a saccharometer, &c. In all cases, however, the principle of its construction is the same, and founded on the obvious property possessed by a body floating upon a liquid of sinking or rising, in proportion as the liquid in which it floats is heavier or lighter; or, in other words, possesses a greater or lesser amount of specific gravity. Hydrometers are graduated in numerous ways; but they invariably consist of an elongated vertical stem, a buoyant bulb, or else a buoyant solid expansion, and a terminal weight, as represented in the accompanying diagram.

Cohesive Attraction is a property which is common to a great variety of bodies. It is most strongly exerted in solids, and in these it is proportionate to the mechanical force required for effecting their disunion. In liquids, it acts with considerably less energy; and in aëriform bodies we have no evidence that it exists at all; for their particles, as will afterwards be shown, are mutually repulsive, and, if not held together by pressure, separate to great distances. The force of this attraction is not only different among different bodies, but in various states of the same body. Thus, in the cohesion of certain metals (steel for instance), important changes are produced by the rate of cooling, by hammering, and by other mechanical operations. Water, also, in a solid state, has considerable cohesion, which is much diminished when it becomes liquid, and is entirely destroyed when it is changed into vapour.

The most important view, in which the chemist has to consider cohesion, is that of a force either counteracting or modifying chemical affinity; for the more strongly the particles of any body are united by this power, the less are they disposed to enter into combination with other bodies. In many cases, a very powerful affinity existing between two substances may be rendered wholly inefficient, by the strong cohesion of one or both of them. Hence it has been received as an axiom, that *the affinity of composition is inversely proportionate to the cohesive attraction.* To the language, however, in which this axiom is expressed, it has been justly objected, that it implies an accuracy of proportion between the forces of cohesion and chemical affinity, which cannot be proved to exist; since all that can truly be affirmed is, in general terms, that the affinity of composition is less effective, as the attraction of cohesion is stronger.

The cohesion of bodies may be overcome by mechanical operations, as by rasping, grinding, pulverising, and other modes of division, which are generally employed as preliminary steps to chemical processes. In some instances, even a minuter division of bodies is necessary than can be accomplished by mechanical means; and recourse is then had to precipitation. Silica, for example, in the state of rock crystal, may be boiled for a long time in liquid potassa without any appearance of chemical action. It may even be bruised to the finest powder, without being rendered sensibly soluble. But when first precipitated from a state of chemical solution, it is readily dissolved by that menstruum, and even by some weak acids.

A valuable process in analytical chemistry depends on the application of this principle, and its remembrance may be facilitated by its introduction in this place. In the analysis of a silicious mineral, after every constituent of which it is made up has been brought into solution, the silica is separated by evaporating the whole to dryness, and adding an acid. Previous to evaporation, the silica was soluble both in acids and alkalies, apparently because its cohesion was reduced to the lowest grade. After

evaporation it is no longer soluble, apparently because the cohesion between its particles has been increased by the contraction due to the evolution of the solvent in which it was held. Hence, in actual analysis, the whole evaporated matters being treated with an acid, every constituent, silica excepted, is dissolved.

Cohesion may be counteracted by heat, applied so as to melt one or both of the bodies, if fusible; or to raise them into vapour, if volatile. Lead and sulphur contract no union, till one or both of them are melted by heat. Arsenic and sulphur are united most effectually, by bringing them into contact, when both are in a state of vapour.

Cohesion may also be counteracted by *solution;* and this is so general a condition of chemical union, that it was formerly received as an axiom, that *bodies do not act on each other, unless one or both are in a state of solution;* a principle, to which the progress of chemical science has since discovered many exceptions.

Solution is a term applied to a very extensive class of phenomena. When a solid disappears in a liquid, if the compound exhibit perfect transparency, we have an example of solution. The expression is applied, both to the *act* of combination, and to the *result* of the process. When common salt, such as is used in cookery, is agitated with water, it disappears; in other words, its solution takes place; and we also term the liquid which is obtained *a solution of salt in water.* This is one of the simplest cases that can be adduced of the efficiency of chemical affinity; for solution is always the result of an affinity between the fluid and the solid which is acted upon, often feeble it is true, yet sufficient in force to overcome the cohesion of the solid. This affinity continues to act, until, at length, a certain point is attained, where the affinity of the solid and fluid for each other is balanced by the cohesion of the solid, and the solution cannot be carried farther. This point is called *saturation,* and the fluid obtained is termed a *saturated solution.*

With respect to common salt, water acquires no increase of its solvent power by the application of heat; but there are various salts with which water, though saturated at the common temperature of the atmosphere, is yet capable of dissolving a further quantity by an increase of its temperature. When a solution, thus charged with an additional quantity of salt, is allowed to cool, the second portion of salt is deposited in a form resembling its original one. In a few instances the solvent power of water is diminished by raising its temperature. Of this, an example is furnished by quicklime, which dissolves more abundantly in cold than in hot water. Some salts, also, have the property of dissolving most abundantly in water of a certain temperature, and of being less soluble either above or below that temperature. Such are the sulphate and seleniate of soda (35 Ann. de Ch. et de Phys. 102).

Crystallization.—To recover a salt from its solution, if its solubility does not vary with the temperature of the solvent, as common salt, it is necessary to expel a portion of the fluid by heat. This constitutes the process of *evaporation.* If the evaporation be carried on very slowly, so that the particles of the solid may approach each other in the way best adapted to them, we obtain solid figures, of a regular shape, called *crystals.* The crystallization of a solid may also take place from that state of fluidity which is produced by heat. Thus several of the metals crystallize on cooling from a melted state; and some volatile bodies, as arsenic, assume, when condensed from the state of vapour, the shape of regular crystals.

In the act of separating from the water in which they were dissolved, the crystals of almost all salts carry with them a quantity of water, which is essential to the regu-

larity of their form, and cannot be expelled without reducing them to shapeless masses. It is termed their *water of crystallization*. Its proportion varies in different salts; in some it is extremely small; in others it constitutes the principal part of the salt, and is even so abundant as to liquefy them on the application of heat, producing what is called the *watery fusion*. In every salt it exists, not in an uncertain but in a definite proportion, bearing in the same salt the same ratio to the solid saline matter, but differing for different salts. The water of crystallization is retained also in different salts with very different degrees of force. Some crystals, which lose their watery ingredient by mere exposure to the atmosphere, are said to *effloresce;* or in some the loss is so complete that they become *anhydrous;* that is, others retain variable quantities of water, according to the hygrometric state of the air. (Ann. de Ch. et de Ph. xxxii. 334.) Other salts, on the contrary, not only hold their water of crystallization very strongly, but even attract more; and, on exposure to the atmosphere, become liquid, or *deliquiate*. The property itself is called *deliquescence*. There are, however, a few salts (as sulphate of potassa and chloride of sodium) which, though their forms are perfectly regular, contain essentially no water of crystallization, but yet hold a very small portion, mechanically retained between the plates of their crystals.

When two salts are contained in the same solution, which vary in their degree of solubility, and which have no remarkable attraction for each other, they may be obtained separate. For by carefully reducing the quantity of the solvent by evaporation, the salt whose particles have the greatest cohesion will crystallize first. If both salts are more soluble in hot than in cold water, the crystals will not appear till the liquid cools. But if one of them, like common salt, is equally soluble in hot and in cold water, crystals will appear, even during the act of evaporation. In this way we may separate nitre from common salt, the crystals of the latter being formed during evaporation; while those of nitre do not appear till some time after the fluid has cooled.

Salts, which are deposited in regular shapes, generally adhere to the surface of the vessel containing the solution, or to any substance, such as pieces of thread or of wood, introduced for the purpose of collecting them. But a still more effectual way of inducing crystallization is to immerse, in the solution, a crystal of the same kind with that which we expect to be formed. The crystal, thus exposed, receives successive additions to its several surfaces, and preserves its form, with a considerable addition to its magnitude. This curious fact was originally noticed by Le Blanc, who has founded on it a method of obtaining large and perfect crystals.

In some instances, the affinity of a salt for its solvent is so powerful, that it will not separate from it in the form of crystals; but will yet crystallize from another fluid, which is capable of dissolving it, and for which it has a weaker affinity. Potassa, for instance, cannot be made to crystallize from its watery solution, but will yet separate, in a regular form, from its solution in alcohol.

To clear away from any crystalline product the *mother water*, as the remaining fluid has been called, Robiquet recommends the transmission, by suction, of a current of air through the crystals. The simplest way of doing this is to place the crystals in a glass funnel, the pipe of which is loosely stopped by a little cotton wool, and then fixed in one of the mouths of a two-necked bottle, the juncture being made as nearly air-tight as possible. A bent tube being also fixed tightly into the other neck, and the air sucked through this tube, the crystals are cleaned in a few seconds.

It is usual with many foreign writers on chemistry to make a distinction between the meaning of the terms *solution* and *dissolution*. By the former, they understand the

mere conversion of a solid into a liquid by some menstruum, or the union of two liquids with each other, without any other change of quality being effected, except as regards the state of cohesion; by the latter, they understand not only the overcoming of cohesion, but the alteration of chemical quality. Thus common soda (carbonate of soda), if treated with a sufficient amount of water, becomes converted into an alkaline liquid, from which, if the water be driven away by heat, carbonate of soda unchanged remains; but if, instead of water, sulphuric acid (oil of vitriol) be used, then the soda is, as before, liquefied, but its chemical constitution is altered; so that, on driving the excess of fluid away, carbonate of soda is no longer reproduced, but a combination of it with sulphuric acid.

The attraction of cohesion is the force which, as we have seen, causes similar particles to become aggregated into a mass. But masses thus generated may be characterized by one of two physical qualities. They may either assume well-defined regular shapes, bounded by planes and angles, or they may be totally devoid of such regular shape. Bodies of the former kind are said to be crystalline; and the mathematical solids which they generate are termed crystals. Those of the second kind are termed amorphous—that is, without form (definite mathematical form understood); and bodies generating such masses are said to be *amorphous*.

A casual examination of solids would lead to the impression that the crystalline state is the exception, not the rule, and that by far the greater number of bodies is amorphous. There is reason to believe, however, that the direct opposite of this is true—that all solids possess the tendency to assume a regularly crystallized condition; and when the reverse obtains, it is due to a variety of interfering causes. Bodies, seemingly the most opposed to the crystalline state, nevertheless can be sometimes made to assume it by artificial means; and many bodies, seemingly amorphous, can, by a treatment hereafter to be described, be demonstrated to contain within their substance crystals in a latent form.

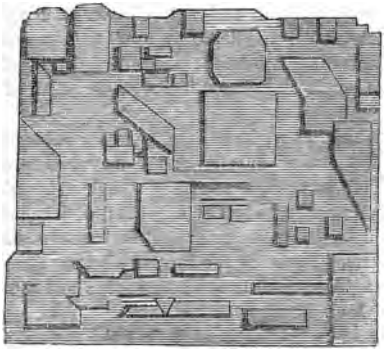
As an example of the former, the simple bodies, sulphur and phosphorus, may be mentioned; neither of which, in its common state, has the appearance of crystallization; sulphur being a well-known hard amorphous substance, and phosphorus soft like wax. Each, however, may be made to crystallize by proper treatment; and so strongly developed is the crystalline tendency in sulphur, that it may be made to crystallize in two different systems.

Carbon may be cited as another instance. In the most usual condition in which this element occurs, namely, as charcoal, it is totally devoid of crystalline aspect. Nevertheless, under modified circumstances, it not only crystallizes, but, like sulphur, crystallizes in two distinct systematic forms. In the diamond, carbon furnishes crystals belonging to a system presently to be treated as the cubic or tessular; and in plumbago it crystallizes in the rhombohedral system.

As examples of bodies not seemingly crystalline, out of which, nevertheless, a crystalline structure may be developed, the following instances may be selected.

The usual form of alum is crystalline; but not unfrequently masses of it, seemingly amorphous, may be observed. If one of these masses be immersed in a limited portion of cold water (about 1500 grains of alum to 15 measured ounces of water), be set by in a quiet place for three or four weeks, and attentively watched, the following phenomenon will be recognised. The alum, being very soluble in water, will begin to dissolve, but not regularly every part of its surface alike, but at intervals portions will be dissolved out, leaving other portions unacted upon by the solvent. Gradually the

remaining portions will be seen to have assumed crystalline forms of octohedrons, and sections of octohedrons in high relief, and of various dimensions. These will have withstood the disintegrating agency of the water, apparently because of the greater permanency imparted to them by that complete exercise of cohesive force which had been employed to generate crystalline forms. This new process of dissection admits of extensive application. Borax in the course of six weeks exhibits eight-sided prisms with various terminations; and other salts may be made to unfold their external structure by the slow agency of water. Carbonate of lime, carbonate of strontia, and carbonate of baryta, give also distinct results when acted upon by weak acids; and even amorphous masses of metals, which have a tendency to assume the crystalline form, such as bismuth, antimony, and nickel, when exposed to very dilute nitric acid, presented at the end of a few days distinct crystalline forms. Large crystals of sulphuret of antimony, as discovered by Mr. Faraday, admirably illustrate this; and it is also Mr. Daniell's mode of displaying crystalline texture. When such a crystal is introduced into a portion of fused sulphuret, it is found to melt down, but not uniformly, for crystals are left more than half an inch long projecting from it. (Quart. Journ. i. 24, and xi. 202; also Journal of Royal Institution, vol. ii.)



In this manner, by employing proper solvents, many bodies, not commonly associated in our minds with the crystalline character, may be shown either to contain crystals, or to manifest such appearances as shall be indicative of that exercise of regular cohesive force which, if further developed, would have ended in crystallization. Thus, if a piece of tough iron wire be exposed to the action of weak sulphuric acid and water, it will not be dissolved on all parts alike, but the phenomenon manifested by the alum will be repeated, although to a less marked extent. Regular crystals will not be developed (although iron is capable of assuming such); but long striæ will appear giving the iron the aspect of a fluted column, and indicating that even in this seemingly amorphous mass the power of cohesion had begun to assume a certain symmetry of agency.

Before proceeding to cite other instances of seemingly amorphous masses developing under proper treatment a crystalline structure, I shall here mention a point of deep practical interest as concerns the semi-crystalline state, which even wrought-iron (cast-iron is obviously crystalline) possesses to a slight extent, and which can be further developed. It is said that a wrought-iron bar, however non-crystalline, and therefore tough, may, by a series of beatings, hammerings, or other concussions, be made to assume the semi-crystalline character. This is what theory would have indicated *a priori*, and is quite consistent with analogies. The importance of being aware of this fact is very great. The tenacity or toughness of iron entirely depends on its freedom from the non-crystalline state; hence the acquisition of this state must necessarily prove detrimental, often dangerous, in all cases involving the use of wrought-iron for engineering purposes. Attention has been chiefly directed to the fact in

reference to the axles of railway carriages, which are said to become brittle after long use, on account of the continuous friction and percussion to which, whilst in use, they are exposed, gradually inducing the crystalline state. This is just what might have been expected, *a priori*. Parallel instances are frequently seen. For example, the non-crystalline or amorphous character of barley-sugar is well-known; yet in this substance the tendency to a crystalline state is so far from being absent, that when set aside for a time, and more especially if exposed to the solar rays, minute crystals first become developed on its surface, imparting a general aspect of opacity. Gradually these crystals extend, penetrating deep into the substance, until the whole stick becomes crystalline. Whilst the barley-sugar was amorphous and transparent it was also tough; now, however, it will be found to have become brittle, and may be fractured by a slight blow, or broken asunder by the application of a slight lateral force.

Brass-wire furnishes another example of the assumption of a crystalline state by an originally non-crystalline body. When new, it is remarkably tough and pliable; yet after it has hung for some time exposed to mutations of temperature, and the agency of chemical fumes, as in a laboratory, for instance, it occasionally becomes so brittle that a very slight force serves to rend its particles asunder. Silver occasionally assumes a precisely similar condition, as may frequently be observed in vessels of this metal used for chemical purposes, and exposed to sudden mutations of heat and cold. Glass, too, although completely amorphous when first made, takes on the crystalline aspect by age. Many specimens of ancient Egyptian, Roman, and Grecian manufacture have come down to us in this condition.

A similar observation has been made by Dr. M'Culloch, as regards the crystalline texture sometimes acquired by certain sorts of sandstone which have suffered long exposure to heat, as forming the hearths of furnaces. Common white arsenic (arsenious acid) also presents a familiar example of an amorphous body changing to a crystalline one. When newly sublimed arsenious acid is usually transparent like glass, and presents a conchoidal fracture; but after the lapse of a certain period it becomes opaque, owing to the formation of innumerable crystals. This change, although usually the result of a considerable time, sometimes takes place suddenly, as Professor Rose has remarked; and in connexion with the sudden change he has mentioned a curious phenomenon. If the vitreous acid be dissolved in hot dilute hydrochloric acid, crystals of the opaque variety are occasionally deposited, a bright flash of light being emitted at the formation of each crystal. If the hydrochloric acid solution be made with the crystalline instead of the vitreous arsenious acid, the peculiar result just mentioned does not take place.

It would appear, then, from a consideration of these instances, that the amorphous state of cohesion is by no means to be considered as the more general tendency of inorganic matter.

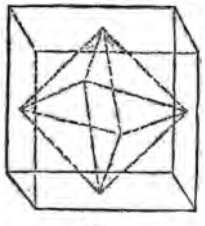
Not alone do many seemingly amorphous bodies gradually assume a crystalline character, but certain crystals have been found to separate themselves after a time into smaller fragmentary crystals, sometimes of a different shape. Thus, if crystals of sulphate of magnesia, or sulphate of zinc, be heated in oil to a temperature of about 126° they become opaque; and on being fractured the particles are found to consist of a multitude of little crystals. (Methuon in Quart. Jour. 1., p. 123; Gregory Watts, Ph. Trans. 1804, p. 279; also Mitscherlich). Prismatic crystals of sulphate of nickel and seleniate of zinc (Brande, Manual, p. 129) when exposed to the sun become opaque, and break up into small octohedrons.

It is necessary to remember that the appellation *a-morphous*, although literally signifying absence of form, is used by writers on crystallography merely to indicate the absence of one quality of form, namely, that defined by straight lines and angles. The quality of form manifested by organic beings, and characterized by curves, is not taken cognizance of by the term amorphous. In general terms we may state that the peculiar exercise of cohesion, which results in the formation of crystals, belongs exclusively to inorganic bodies, and is incompatible with the existence of life. Hence a crystal may, in general terms, be stated as the most perfect manifestation of a dead, as an organ is the highest manifestation of a vital or living, being.

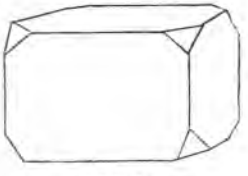
In ordinary language, the term crystal is associated with transparency; in the language of science, however, this idea is much extended. A crystal need not be transparent, nor colourless; on the contrary, it may be of any degree of opacity and of colour, the only quality necessary for it to possess, in order to come under the denomination of a crystal, being that of filling a space bounded by right lines and angles.

The next important point to be investigated, in the study of crystals, is the different amount of cohesive force exercised in different parts of a crystal. Thus, for instance, it is well known to lapidaries that a crystallized precious stone cannot be cut with equal facility in all directions. It is equally well known to mineralogists, also, that crystalline minerals, when let fall, or struck at random with a hammer, do not break irregularly, as might without trial have been supposed, but shiver into geometrical fragments, having some close relation to the original form. In this way mineralogists have dissected crystalline bodies, so to speak, with the object of discovering the primitive forms of which they were assumed to be composed.

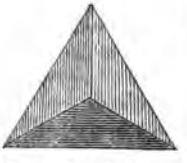
The usual figure of Derbyshire or Fluor-spar, is a cube, which, if we strike with



Cube.

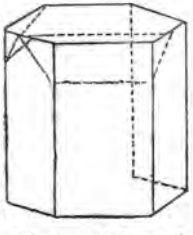


Octahedron.



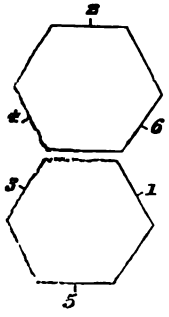
Pair of Tetrahedrons.

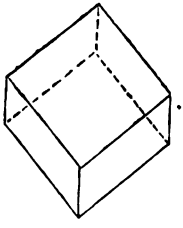
a hammer in various directions, will only be found to yield readily in one series. The solid angles readily chip off, but it will be impossible to strike or cut off regular slices parallel with the cubic faces. Proceeding in this way, dissecting off the angles or corners by degrees, we develop a new series of forms. First of all we destroy any, or all, of the four solid angles of the cube, replacing them by plane triangles—increasing in area as the dissection proceeds—until we end by generating a figure with eight sides, the octahedron with square base, and which may be conceived to be the result of placing together, base to base, a pair of tetrahedrons.



One usual form of calc spar is a six-sided figure, with plane ends (the hexagonal prism). If we proceed to dissect a crystal of this kind we shall find another law of

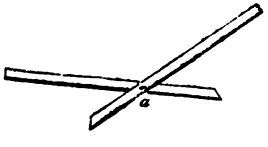
cleavage to be manifested. Here, it is not the solid angles which yield to the blow, nor all of the sides indiscriminately, but the cleavage takes place as follows:—Of the six edges on the superior plane of the crystal, three yield in a slanting direction; and out of the six edges on the inferior plane three also yield in this manner; but in a condition of double alternation, that is to say, numbering the corresponding superior and inferior planes, as in the diagram; those of the superior plane which yield corresponding with the numbers 2 4 6; those of the inferior plane which yield will be 1 3 5. Proceeding in this way with the dissection, we ultimately arrive at what has been called the primitive form of the Iceland spar, namely, a rhombohedron, or solid figure, all of whose sides are parallel, and whose planes are rhombs; moreover, the cohesive force which determines the formation of this rhombohedron is so nicely balanced that the angles which measure its superficies are 105° 5′; and inasmuch as no known substance crystallizes in rhombs of exactly this angle, a mineralogical characteristic of Iceland spar is obtained. Other bodies crystallize in obtuse rhombohedrons; thus, for instance, pearl-spar, iron-spar, and tourmaline crystallize in rhombohedrons; but the rhombohedrons in all these cases vary as to the measurement of the angles. The primitive angle of pearl-spar is 106° 5′, of iron spar 107° (Wollaston, Phil. Trans., 1812), and of tourmaline 113° 10′.



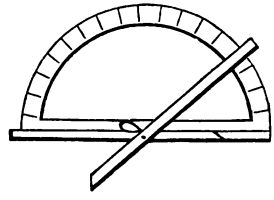


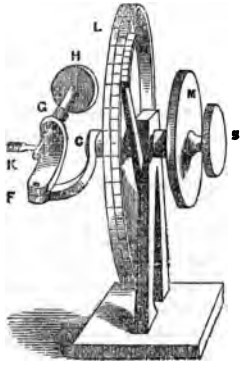
In stating these measurements, however, it is necessary to remark that they are only correct for a mean temperature of 60° F. It will be shown hereafter that it is a property of all crystals, save those belonging to the tessular or cubic system, to expand unequally on being heated, and, therefore, to cause an angular variation. Mitscherlich (Ann. de Ch. et Phys. xxv., 108) has remarked that the angular variation of Iceland spar, between the temperatures of 32° F. and 212°, differs to the extent of 8° 5′; that is to say the smaller axis of the rhomboid dilates more than the longer, thus causing the rhombohedron to approach the cubic form.

Although every body susceptible of crystallization assumes a limited number of crystalline forms, which generally belong to one particular system for each body, yet it is not a fact, as was once supposed, that identity of crystalline form bespeaks identity of chemical composition. The recognition of crystalline forms, however, by the exact measurement of crystalline angles, is so necessary a part of chemical science that a description of the instruments — termed goniometers — for effecting this may not be out of place here, although the science of Crystallography has been so largely dwelt upon in another department of this work, by Professor Tennant and the Rev. W. Mitchell, as to render any lengthened details unnecessary here. Carangeot's goniometer, represented by the following wood-cut, consists of two metal rulers fastened together at the pivot *a*, in such a manner as to constitute a pair of proportional compasses in the angle formed by the divergent legs of which the angular faces of the crystal to be measured is put, care being taken that the legs of the compasses touch the



faces of the crystal in lines perpendicular to the intersection of these faces. When the legs have been thus adjusted the instrument is removed, and the axis *a* being brought into coincidence with the corresponding point on the plane, joining the two ends of the semicircular protractor, and in direct parallelism with the plane itself, the angular value of the two sides under measurement may be read off. This instrument, although simple in its operation, is obviously incorrect for the greater number of crystals; inasmuch as those which are not large and perfectly formed are ill-adapted for measurement by this plan of operation. A far more correct instrument was devised by Dr. Wollaston. Its agency depends not upon the principle of measurement by contact, but by taking as radius the ray of light reflected from any crystalline face (Phil. Trans., 1809). The following description of Wollaston's goniometer is taken from the new edition of Phillip's Mineralogy, by Professor Miller and Mr. Brooke:





"A graduated circle, L, the divisions of which may be read off to minutes by means of a vernier, N, is fixed on a hollow axle which may be turned round by the milled head, M. An axle, CS, passing through the hollow axle of L, and which either turns with the circle L, or may be turned independently by means of the milled head at S, carries a crooked arm GF. The part FG is connected with CF by a joint which permits it to turn round an axis perpendicular to CS, passing through CS, produced, and has a collar at G in which the pin HK turns and slides, with its axis perpendicular to the axis of FG, and passing through the point in which SC, produced, intersects the axis of FG. The crystal is fastened by means of a soft cement to a thin plate of metal fixed in a slit at K.

In order to measure the angle between two faces of a crystal, proceed as follows:—Let *p q* be two faces of a crystal. Make the intersection of *p q* parallel to the axis of the circle, and as nearly coincident with it as possible, by means of the angular motion of F G, and the angular and sliding motion of H K. Place the instrument upon a firm stand, and let A B be two signals in a plane passing through a point K in the intersection of the faces *p q*, and perpendicular to the axis of the circle. Turn the circle till the image of one of the signals A, seen by reflection in the face *p*, coincides with B viewed directly, and read off the arc at which zero of the vernier stands. Now turn the circle until the image of A, seen by reflection at *q*, coincides with B, seen by direct vision, and read off the arc at which zero of the vernier stands. The difference of the two readings will measure the angle between the faces *p q*. If a face *r* belong to the zone of *p q*, it will be parallel to the axis of the circle, and therefore in some one position of the circle the image of A, seen by reflection in *r*, will coincide with B seen directly. Hence, in order to find the faces which belong to the zone containing two given faces, we must adjust the crystal as for the purpose of measuring the angle between those faces, and then, while the circle makes one revolution, observe the faces

that afford by reflection images of A passing through B. In order to make A B K the plane through the two signals, and the crystal perpendicular to the axis of the circle, turn the stand of the instrument, or move A till the image of A, seen by reflection in the plane surface of the circle, or in any bright plane surface fixed parallel to it, coincides with a point A seen directly; the distance of which from A, in a line parallel to the axis, is equal to twice the distance of the crystal from the plane of the circle, or from the reflecting surface. Let a solid, having two bright parallel surfaces, be fixed in the place of the crystal, and adjusted till the image of A, seen by reflection in either surface, describes the same path while the circle revolves, and place the lower signal B in the path traced out by the image of A. Having thus made the plane A B K perpendicular to the axis of the instrument, the intersection of the faces *p q* is known to be parallel to the axis, when, on turning the milled head S, the images of A, seen by reflection in *p q*, are observed to pass through B. The adjustment of the edge *p q* is most easily made by cementing the crystal to the plate K with one of the two faces *p*—for example, nearly parallel to the plate, which is to be fixed in the slit at the end of H K, so that the intersection of *p q* may be nearly perpendicular to H K, and therefore H K nearly perpendicular to C S. By turning H K round its axis, the path of the image of A, seen in *p*, may be made to pass through B; and then, by turning F G on its axle at F, the path of the image of A, seen in *p*, may be made to pass through B; and then, by turning F G on its axle at F, the path of the image of A, seen in *q*, may be made to pass through B. Should the latter adjustment disturb the former, the process must be repeated. The instrument, as it is usually constructed in this country, is encumbered with a spring stop, which allows the circle to be turned in one direction only, and serves to fix it, not very accurately, at 0 or 180°. This should be removed by taking out the screws which fasten it.

In using the instrument, it will be found most convenient to turn it in such a direction that the degrees increase in passing from one face to the next.

The distances of the two signals from the crystal should be nearly equal, and not less than six or eight feet. The more distant the better. The upper signal, when the observations are made in the day-time, may be a narrow black bar, or a horizontal slit in a screen placed in the upper part of a window, parallel to the axis of the circle; and the lower signal, a white line on a black ground, also parallel to the axis of the circle. In some cases an image of the sun, formed by a lens of short focal length, or a small round hole in a screen, through which the light of the day is seen, may be used with advantage for the upper signal. If we make our observations at night, two narrow slits in screens (through one of which is seen the flame of a candle, and through the other a sheet of paper illuminated by a candle placed behind it), answer extremely well for the upper and lower signals respectively.

The best bright signal is obtained by reflecting the light of the sun from a plane mirror, or heliostat, through a triangular opening in a plate of metal, which, by means of a slider, may be diminished or increased according as the faces of the crystal are more or less perfect. The faint signal may be a horizontal slit in a plate of metal, illuminated by a sheet of white paper placed behind it, viewed by reflection in a mirror of black glass. The signals A B may then be nearly on a level with the eye of the observer, and need not be more than six inches distant from each other. In making our observations, we find that the image of A, seen by reflection in a face of the crystal, is made to coincide with the image of B, seen by reflection in the mirror, which should make an angle of about 40° with a horizontal plane. When the mirror is attached to

the foot of the goniometer, any unsteadiness, in the support of the goniometer, will not affect the accuracy of the observations.

It is not essential that the axis of the goniometer should be horizontal. A goniometer with a vertical axis, though perhaps not quite so convenient in use, is free from some sources of inaccuracy to which a goniometer with a horizontal axis is subject.

When the points of *p q*, at which the reflections take place, are not equally distant from the axis of the circle, the angle through which the circle revolves between the two observations will differ slightly from the angle between the faces *p q*. This error may be eliminated when the angles A B are nearly equidistant from the crystal, by turning the instrument half round in azimuth, and repeating the observation. A mean of the two results will be free from the error arising from the eccentricity of the points at which the reflection takes place.

When either of the faces is large, it should be blackened over, except at the point where it is intended the reflection should take place. Any error that may arise from imperfect centring of the circle, will be eliminated, if the observations be repeated, so that observations at a given face be made with zero of the vernier at points of the graduated circle, distant nearly 180° from each other. In many crystals not belonging to the cubic system, Mitscherlich discovered that the angles between certain faces vary slightly with the temperature of the crystal; thus the directions of the cleavages of calcite, which, at the ordinary temperature of the atmosphere, make angles of 75° 55′ with each other, become more nearly right-angled by 8° 5′, when the temperature of the crystal is increased to 212° Fah.

Practical Applications.—Hitherto the theory of crystallization has been considered abstractedly; it now remains, therefore, to discuss certain useful applications of crystallographic knowledge. *To the mineralogist* an acquaintance with the crystallographic forms, assumed by different mineral groups, will be too obvious for comment; and although, contrary to the doctrine of Haüy, it be not true that identity of crystalline form is infallibly indicative of identity in chemical constitution for all crystals not belonging to the cubic system, yet a familiar acquaintance with crystallography imparts a large and readily available knowledge of mineral species. This kind of knowledge is of particular use in cases involving the investigation of valuable crystalline mineral specimens, which it would be undesirable to destroy by comminution, for the purpose of chemical experiment. Take, for instance, the case of the diamond and rock crystal. To the uninitiated eye these substances bear a remarkable similarity. Both are colourless, usually; both are endowed with high refractive powers; both may be found in the same locality. In the rough state, rock crystal possesses the greater beauty; and many persons have been deceived as to the real quality of these mineral crystalline forms. Professor Tennant relates an instance in his lectures of a Californian gold-seeker. Having found, in the prosecution of his workings, a large rock crystal, he was offered several hundred pounds for it on the spot, which he refused, and hurried home, on the supposition that his treasure was a diamond. Arrived in England, he at length found that the crystal was not worth so many shillings as he had been offered pounds for it. This mistake might readily have been obviated, had the finder known that the diamond belonged to the cubic system, and rock crystal to the rhombohedral. Accordingly, whilst the diamond crystallizes in cubes or their derivatives, rock crystal affects the shape of prisms, having six sides, terminated by similarly sized pyramids.

To the analytical chemist a knowledge of the forms in which different substances

crystallize is of the highest importance, as enabling him to ascertain the presence of many bodies whose peculiar crystalline aspect may have been previously known; as also frequently to effect the separation of one body from another, even though both should be susceptible of crystallization. The student may form an idea of the ready means with which certain salts may be distinguished by their crystalline aspect by dissolving in three separate tubes of distilled water respectively a little chloride of sodium (common salt), sulphate of magnesia (Epsom salt), nitre (nitrate of potash), and Glauber's salts (sulphate of soda), and evaporating a few drops of each of these solutions on respective pieces of glass very slowly. For this purpose the slip of glass may be held about six inches above the flame of a candle, or placed in some warm place to which dust cannot gain access. As the process of evaporation goes on, so will crystals become deposited; and, however small, may be readily discriminated by means of a lens of sufficient power. In these experiments it will be remarked that the solution of common salt deposits its crystal first—a circumstance of great practical importance in many operations, and which will be further adverted to hereafter. Appended is a sketch of the appearance represented by this series of four:—

Common Salt.

Epsom Salts.

Nitre.

Glauber's Salts.

Thus it is evident an acquaintance with crystallography may become an aid to the chemist. Frequently he has to pursue an elaborate investigation for the discovery of minute portions of white arsenious acid; and here again a knowledge of the form in which the substance crystallizes is in the highest degree necessary. If only the thousandth part of a grain of arsenious acid be deposited towards the closed end of a small glass tube, and cautiously heated by means of a spirit-lamp, the arsenious acid will sublime farther up in the tube, in the form of octohedral crystals, easily recognised by means of a lens. No other substance deposits similar crystals under similar conditions; hence the test becomes extremely valuable, more especially as it involves no loss of the material—a most important point in cases of medico-legal investigations, wherein the amounts operated upon are necessarily minute, and their preservation, to take before a jury for demonstration, is required.

Hence it is evident that a familiar acquaintance with crystalline forms is of great importance to the chemist as a means of discrimination. Of not less importance is it as a means of separation, concerning which I shall now append some exemplifications. In the manufacture of gunpowder, it is necessary that the nitre employed should be freed, to the greatest practicable degree, from the common salt with which it naturally occurs, inasmuch as common salt has the property of attracting water from the atmosphere, and deliquescing; thus continually rendering substances damp with which it may come into contact. This separation of common salt from nitre is effected by taking advantage of the different crystallizing powers of these two substances. If a nitre solution be mingled with a solution of common salt, and the compound mixture be evaporated, the common salt will be deposited first, and may be separated, leaving

the nitre solution pure. This is the process had recourse to in practice; and its efficiency depends on the circumstance that nitre is more soluble in hot than in cold water; whereas common salt is equally soluble in water, hot or cold.

The iodine manufacture affords another instance of the application of the same principle. When certain varieties of sea-weed are incinerated, their ashes are found to contain various salts, which may be dissolved out by lixiviation. On subjecting the lixiviated fluid to evaporation, carbonate of soda crystallizes and deposits first. Indeed kelp was formerly prepared solely on account of the carbonate of soda it yielded; although for a long time past this substance has been obtained much more economically as a result of the decomposition of common salt. When the carbonate of soda has been entirely separated, there remains behind a solution containing various other salts, of which the iodide of sodium is the chief. On carrying the evaporative process farther, this too may be obtained. Iodide of sodium, or the liquor containing it, is now the chief source of iodine.

A very beautiful application of the laws affecting crystallization, by which a crystallizable substance is separated from its impurities, may be recognised in the process of sugar-refining. Metallic cones, ranged apices downward, each apex having a small plugged orifice, are filled with a magma of dark-coloured sugar; the darkness is caused by molasses, in which, after the lapse of some hours, the sugar crystallizes, and from which the crystals have to be freed. This is accomplished in the following manner:—

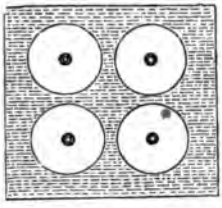
Each cone is put to stand on a corresponding pot, the plug in the apex of the cone having been previously removed. In this way a very large portion of the treacle drains off. Not all, however, inasmuch as the sugar, if scooped out, would be more or less yellow. Hence the crystals have to be *washed* clean; and great ingenuity has been shown in devising an efficient means of accomplishing this. It is evident that water would be inapplicable, since this liquid would dissolve the sugar. Alcohol might answer the purpose tolerably well, if it were sufficiently cheap to be employed. Indeed alcohol is so employed for this purpose in the East Indies. A still more efficient and far more elegant plan, is generally adopted in British and most European refineries. Instead of using alcohol, which at the utmost can only dissolve out the treacle and leave vacuities in its place, an already saturated and colourless solution of sugar is employed, which, gradually forcing its way from base to apex of the cone, and penetrating between the loosely impacted crystals, not only forces the molasses away, but adds a fresh coating of sugar to the crystalline nuclei already existing.

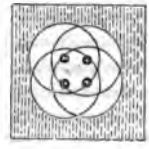
Inasmuch as the formation of a crystal depends on the most perfect agency of cohesive force, in deference to the operation of which particles of matter are impelled into lines and planes referable to determinate axes of energy, it necessarily follows that the most perfect conditions for effecting crystallization are those which secure a perfect freedom of motion amongst themselves of the particles to be aggregated; and

although certain solids may, as we have seen, change from the amorphous to the crystalline state without passing from the solid state, yet these furnish only so many exceptions to the general law. Accordingly the three grand preliminary conditions, to the ultimate formation of crystals, are (*a*), solution; (*b*), fusion; (*c*), vaporization. Of these three conditions examples of the first and the third have already come under our notice indirectly, and the second has been adverted to.

More detailed observations concerning all these will now be given.

The process of solution accomplishes the separation of aggregated particles by the interposition of the solvent between them, in such a manner that the particles are removed beyond the sphere of each other's cohesive attraction,—a condition which is represented conventionally by the appended diagram. The central dots are assumed to represent the particles themselves; the circles surrounding them to define the extent of the force of cohesive attraction for each particle; and the horizontal parallel lines to represent the fluid of solution. Under these theoretical circumstances it will be manifest that the particles cannot aggregate until so much of the solvent shall have been removed as shall bring the particles within each other's sphere of attraction; when, in accordance with the postulate laid down, the particles should cohere.





In most cases the power of solution, manifested by a liquid, does not depend upon the quantity employed alone, but also upon the degree of heat to which it may have been raised; whence it follows that, as a general rule, bodies are more soluble in a given liquid hot, than when the same liquid is cold. In such instances crystallization always takes place most readily as the solvent is cooling; and certain substances, of strong crystalline character, are, nevertheless, totally incapable of crystallizing in a temperature at which the solvent boils under the ordinary pressure of the atmosphere. This is the case with sugar. It is highly crystallizable in its nature; but if dissolved in water, and the water dissipated by evaporation at the boiling temperature, it obstinately refuses to crystallize. If, however, a current of cold air be continuously blown through a boiling solution of sugar, so as to lower the temperature of the mass to about 180° F., then crystallization readily takes place. This principle has been taken advantage of in the manufacture of sugar; but its efficiency is less by far than that of the vacuum-pan,—an instrument which will be hereafter described.

The problem of removing a liquid, by means of evaporation, from a crystallizable body held in solution (in order that the latter may crystallize, without, at the same time, employing a temperature detrimental to the crystallizable material), is one that has frequently to be solved in chemical practice, and its successful accomplishment is based upon the following considerations. The tendency of a liquid to evaporate is due partly to the recognizable repulsive effects of heat, and partly to the natural repulsion (which may be due to heat also) existing between the particles of fluids themselves. The agency repressive to evaporation is atmospheric pressure. Hence, to the extent that we remove atmospheric pressure from a liquid, to the same extent do we tend to promote its evaporation. Many volatile liquids, such as ether, chloroform, &c., actually boil when atmospheric pressure is removed from them; so prone are they to evaporate; and, although water does not boil under these circumstances, yet its evaporative

tendency is so much increased that it will boil on the application of a very low degree of heat. These facts, more fully adverted to in the chapter on vaporization, suggests the basis of effecting the crystallization of solutions, the crystallizable substance contained in which would be damaged by exposure to an increase of heat. The solutions are placed aside in vacuo, and a material being placed near them capable of absorbing the vapour as it rises, a continued vacuum, or rather an approach to a vacuum, is maintained. Generally speaking, the vapour thus required to be absorbed is that of water; hence some hygroscopic material is the proper absorbent substance. Sulphuric acid is most commonly employed for this purpose; and the method of using it will be fully described under the head of Evaporation.

The process of fusion accomplishes the separation of aggregated particles, not in consequence of the interposition of a solvent, but in consequence of the repulsive effects of heat, which indeed we are almost warranted in calling the universal solvent, inasmuch as we are not aware of any one substance which cannot be liquefied or converted into vapour by the application of a sufficient amount of heat. Although the seeming effect of fusion is the generation of amorphous masses, this is more specious than real. Most substances, the products of fusion and cooling, although apparently amorphous, yet develop a crystalline texture more or less perfect when subjected to the corroding, or dissecting agency of a proper solvent, just as alum was found to unravel a similar texture when exposed to the solvent agency of water. In certain cases, not only may these crystals be dissected out from the cold mass in which they have become enveloped, but they may be obtained at a previous stage; for the cooling mass does not cohere homogeneously, but the first solid portions are crystals surrounded by the yet liquid material, which latter may be dexterously poured away, leaving the crystals perfect. Bismuth and sulphur are very susceptible of being thus operated upon, and their crystalline texture demonstrated. If either of these be melted in an iron ladle, and the melted mass set aside until a crust forms on the surface, and this crust be perforated with two holes—one to admit of the air entering, the other to admit the issue of the yet unsolidified material when the ladle is inverted—there will be obtained, in either case, a hollow segment of a sphere crusted over in all directions, but containing variously ramified crystals within. If now the flat surface of the crust be chiselled off, the underlying crystalline forms will be laid bare. This means of obtaining crystals, although beautifully illustrative of a principle, is, nevertheless, but seldom taken advantage of in practice.

The process of vaporization will be recognised, on reflection, to furnish the same preliminary conditions to crystallization as that of solution, and that of fusion; that is to say, the freeing of particles from the restraint of motion amongst themselves, which the force of cohesion opposes. Camphor, for example, is prone to assume the crystalline state; but, if aggregated too rapidly, it takes on the amorphous appearance. If, however, one of these amorphous pieces of camphor be very gradually vaporized or sublimed, the volatile particles condense in regularly crystallized forms. This phenomenon may frequently be seen to have resulted from the exposure of druggists' camphor show-bottles in a sunny window. Camphor will, after a time, sublime in crystalline spangles. In this instance, moreover, the crystals will be seen to have collected in that part of the bottle nearest the light.

The substance, iodine, offers another familiar example of a body whose vapour readily assumes the crystalline condition. If some powdered iodine be put into a glass flask, and gently heated, first violet coloured vapours, characteristic of iodine, will be

seen to ascend. Soon these vaporous particles will aggregate in the upper part of the flask, and, eventually, well-formed crystals of iodine will be evident.

Whatever be the method resorted to for the development of crystals, whether by evaporation (sublimation) of the solid to be crystallized—whether by slow cooling, or by evaporation of the liquid in which the substance to be crystallized has been dissolved, one grand principle has to be borne in mind. The operation must be so slowly conducted, that the particles to be crystallized may have the freest power to move amongst themselves slowly and tranquilly; otherwise perfection in the resulting crystals cannot be attained, and a solid, more or less amorphous, will result. In a great majority of instances, the means of effecting crystallization resorted to by the chemist is that of evaporation of the solvent. I shall therefore subjoin a few practical remarks, having special reference to that operation. On this head, no invariable rule of procedure can be given, inasmuch as the exact steps of the evaporative operation vary with the nature of the salt to be obtained. If a salt be equally soluble in cold and in hot water, as is the case with common salt (chloride of sodium), then perfect crystals may be obtained, even during the pocess of boiling; which is to be regarded as manifesting the highest exercise of evaporative energy. If, however, as is more frequently the case, the salt is more soluble in hot than in cold water, then the best general rule that can be given is, to carry on the evaporative process slowly, until a pellicle forms on the surface of the liquor; then to put the solution aside in a cool place, allowing it to remain perfectly at rest. Occasionally rods of glass or wood, filaments of string, &c., are put into a solution from which crystals are about to be deposited, with the object of thus affording nuclei on which the first crystalline particles may aggregate. This, however, is rather a practice followed in certain chemical manufactures on the largest scale, than in the chemical laboratory. Another good plan, when weighed results are not required, consists in dropping into the solution, which is about to deposit its crystal, a few crystals of the same kind already formed. Under the head of individual crystalline bodies, will be appended all such further remarks as may be necessary for effecting their crystallization.

OF CHEMICAL AFFINITY, AND THE GENERAL PHENOMENA OF CHEMICAL ACTION.

Chemical affinity, like cohesive attraction, is effective only at insensible distances; but it is distinguished from the latter force, in being exerted between particles or atoms of *different kinds*. The result of its action is not a mere aggregate, having the same properties as the separate parts, and differing only by its greater quantity, but a new compound, in which the properties of the components have entirely or partly disappeared, and in which new qualities are apparent. The combinations effected by chemical affinity are permanent, and are destroyed only by the interference of a more powerful force, either of the same or of a different kind.

As a general exemplification of chemical action, we may examine that which takes place between potassa and sulphuric acid. In their separate state, each of these bodies is distinguished by striking peculiarities of taste, by great causticity, and by other qualities. The alkali, on being added to blue vegetable infusions, changes their colour to green, and the acid turns them red. But if we add one substance to the other, very

cautiously, and in small quantities, examining the effect of each addition, a point will be attained at which the liquid possesses neither acid nor alkaline qualities; it may now be safely applied to the tongue—the taste is a bitter one—and the mixture will produce no effect on blue vegetable colours. Here, then, the qualities of the constituent parts, or at least some of their most important ones, are destroyed by combination. When characteristic properties thus disappear, the bodies combined are said to saturate each other; and the precise term at which this takes place has been called the point of saturation. It is advisable, however, to restrict this expression to weaker combinations, where there is no remarkable alteration of qualities, as in cases of solution; and to apply to the results of more energetic affinities, when attended with loss of properties, the term neutralization.

At the same time that the properties of bodies disappear on combination, other new qualities, both sensible and chemical, are acquired; and the affinities of the components for these substances become in some cases increased, in others diminished in energy. Sulphur, for example, is destitute of taste, smell, and action on vegetable colours; and oxygen gas is, in other respects, equally inefficient. But one of the compounds of sulphur and oxygen is intensely acid; the minutest particle instantly reddens blue vegetable infusions; and the acid is disposed to enter into energetic combination with a variety of bodies, for which its components evinced no affinity. Facts of this kind sufficiently refute the opinion of the older chemists, that the properties of compounds are *intermediate* between those of their component parts; for, in instances like the foregoing, the compound has qualities, not a vestige of which can be traced to either of its elements.

It is not, however, in all cases that the change of properties is so distinct and appreciable by the senses, as in the instances just described. In some examples of chemical union, the change is scarcely perceptible to the eye or the taste, when the chemist is nevertheless certain that combination must have taken place. This occurs chiefly in the mixture of saline solutions with each other, where a complete exchange of principles often ensues, without any evident change of properties. Examples of this kind cannot, however, be understood, till the subject of complex affinity has been first elucidated.

The existence of chemical affinity between any two bodies is inferred, therefore, from their entering into chemical combination; and that this has happened, a change of properties may be considered as a sufficient proof, even though the change may not be very obvious, and may require accurate examination to be perceived at all.

The proof, which establishes the nature of chemical compounds, is of two kinds, *synthesis* and *analysis*. Synthesis consists in effecting the chemical union of two or more bodies; and analysis in detaching them from each other, and exhibiting them in a separate state. But it is seldom that we can separate two bodies from each other without employing a third, and thus forming some fresh compound. When this new compound is one of known composition, the evidence of analysis is still equally complete. When we have a compound of two or more ingredients, which are themselves compounded also, the separation of the compounds from each other may be called the *proximate analysis* of the body; and the further separation of these compounds into their most simple principles, its *ultimate analysis*. Thus the proximate analysis of sulphate of potassa consists in resolving it into potassa and sulphuric acid; and its ultimate analysis is effected by decomposing the potassa into potassium and oxygen, and the sulphuric acid into oxygen and sulphur.

When the analysis of any substance has been carried as far as possible, we arrive at its most simple principles, or *elements*. By the expression *element* we are to understand, not a body that is incapable of further decomposition, but one which has not yet been decomposed. The progress of chemical science, for several centuries past, has mainly consisted in carrying still farther the analysis of bodies, and in proving those to be compounded which had before been considered as elementary.

At present chemists are acquainted with sixty-two or sixty-three* elementary bodies, the names of which, as well as their symbolical contractions, are appended:—

Aluminium	Al.	Nickel	Ni.
Antimony	St. (Stibium).	Niobium	Nb.
Arsenic	As.	Nitrogen	N.
Barium	Ba.	Norium	Nr.
Bismuth	Bi.	Osmium	Os.
Boron	B.	Oxygen	O.
Bromine	Br.	Palladium	Pd.
Cadmium	Cd.	Pelopium	Pl.
Calcium	Ca.	Phosphorus	P.
Carbon	C.	Platinum	Pt.
Cerium	Ce.	Potash	K. (Kalium).
Chlorine	Cl.	Rhodium	R.
Chrome	Cr.	Ruthenium	Rt.
Cobalt	Co.	Scheelium	W. (Wolfram).
Copper	Cu.	Selenium	Se.
Didymium	D.	Silicon	Si.
Donorium	Do.	Silver	Ag.
Erbium	E.	Sodium	Na. (Natrium).
Fluorine	F.	Strontium	Sr.
Glucinium	G.	Sulphur	S.
Gold	Au. (Aurum).	Tantalum	Ta.
Hydrogen	H.	Tellurium	Te.
Iodine	I.	Terbium	Tr.
Iridium	Ir.	Thorium	Th.
Iron	Fe.	Tin	Sn. (Stannum).
Lanthanium	La.	Titanium	Ti.
Lead	Pb.	Uranium	U.
Lithium	L.	Vanadium	Va.
Magnesium	Mg.	Yttrium	Y.
Manganese	Mn.	Zinc	Zn.
Mercury	Hg.	Zirconium	Zr.
Molybdenum	MO.		

Beside the alteration of properties, which usually accompanies chemical action, there are certain other phenomena, which are generally observed to attend it.

1st. In almost every instance of chemical union, the *specific gravity* of the compound is greater than might have been inferred from that of its components; and this is true both of weaker and more energetic combinations. When equal weights of water and sulphuric acid are made to combine, the specific gravity of the resulting liquid is not

* The existence of Donarium, as a separate element, is doubtful.

the mean, but considerably greater than the mean; this law extends also to solids. But, though general, it is not universal; for in a very few instances, chiefly of aëriform fluids, condensation does not attend chemical union; in the combination of some metals with each other, even the reverse takes place; the compound being, in a few cases, specifically lighter than might have been expected, from the specific gravity of its elements, and their proportion to each other.

2ndly. When bodies combine chemically, it may be received as a general fact, that their *temperature* changes. Equal weights of oil of vitriol and water, both at the temperature of 50° of Fah. are heated, by sudden mixture, to considerably above 212°. In other examples a contrary effect takes place, and a diminished temperature, or, in other words, a production of cold, is observed. This is all that it is at present necessary to state on the subject, which will be more fully considered when we come to treat of caloric.

3rdly. The forms of bodies are often materially changed by chemical combination. The solids may, by their union, become fluid; or two fluids may become solid. Solids are also often changed into aëriform fluids; and, in many instances, the union of two airs, or gases, is attended with their sudden conversion into the solid state. By long exposure of fluid quicksilver to a moderate heat, we change it into a reddish scaly solid; and, by heating this solid in a retort, we obtain an aëriform fluid, or gas, in considerable quantity, and recover the quicksilver in its original form.

4thly. Change of colour is a frequent, but not universal, concomitant of chemical action. In some cases brilliant colours are destroyed, as when chlorine is made to act on solution of indigo. In other instances two substances, which are nearly colourless, form, by their union, a compound distinguished by beauty of colour, as when liquid potassa is added to very dilute syrup of violets. Certain colours appear also to belong essentially to chemical compounds, and to be characteristic of them. Thus 100 parts of quicksilver, and 4 of oxygen, invariably give a black compound; and the same quantity, with 8 parts of oxygen, afford as invariably a red compound.

Proportions in which Bodies Combine.—Certain leading points of distinction existing between the three forces, gravitation, cohesion, and chemical affinity, have been already pointed out. There is another especially characteristic of affinity, and which has been purposely deferred until this opportunity—namely, the proportions in which bodies combine.

On reconsidering the conditions under which gravitation and cohesion are exercised, it will be evident that the operation takes place between any portions of ponderable matter without limit. Thus in the case of gravitation, all matter, of whatever weight (*i. e.*, of whatever number of ponderable particles), is attracted towards the nearest centre of preponderating gravitation—that is to say, for all cases of terrestrial observation towards the centre of the earth.

Again, referring to the circumstances under which the attraction of cohesion exercises itself, we shall find that any conceivable amount of similar particles may unite to any other conceivable amount, and constitute a mass.

As regards the exercise of affinity, or chemical attraction, it is otherwise; not only must the particles which it is desired to associate be of the proper kind, but they must bear to each other a particular ratio, or else combination does not take place. As a simple illustration of this proposition, the composition of water may be cited. This liquid may be decomposed by various means, to be described hereafter. The most convenient process, however, is by means of voltaic electricity. If any quantity of

water be taken and decomposed into its two constituent gases, oxygen and hydrogen, the former will be to the latter in the ratio by weight of eight to one, and in the ratio by measure of one to two.

Such is the composition of water, as made known to us by analysis, and of which synthesis affords a confirmation. If two measures of hydrogen be mixed with one measure of oxygen, and ignited by means of the electric spark, the result is water.

The combination, it will be remarked, has taken place in the exact ratio.

Hydrogen	1	By weight.
Oxygen	8	
Hydrogen	2	By measure.
Oxygen	1	

If, for the sake of experiment, nine parts by weight of oxygen were mingled with one part by weight of hydrogen, then the ninth, or additional part, would not enter into combination, but would remain behind in the gaseous form. If one and a half parts of hydrogen were mixed with eight of oxygen, and inflamed, then the additional half would not combine. Indeed, no combination, except that of water, can be formed by the direct mixture and explosion of oxygen and hydrogen gases; and the composition of water is fixed and invariable. By having recourse to an indirect method, a second compound of hydrogen and oxygen may be developed—viz., the peroxide of hydrogen; and its composition is found to be one part by weight of hydrogen combined with sixteen parts by weight of oxygen. Between these two there is no intermediate composition.

The study of the ratios in which oxygen and hydrogen combine, furnishes an instance of definite proportionality, in which respect the attraction of affinity is seen to differ from that of gravitation, and of cohesion. Definite proportionality may be said to be the great characteristic of chemical combinations. Seeming exceptions to this generalization will be presently cited; but they are probably not real exceptions. An extremely probable hypothesis, if accepted, will refer them at once to the category of definite proportional compounds; and if the hypothesis be not received, still the anomalous cases will be found to correspond with the least energetic operation of chemical affinity, those so ill characterized that they probably should be referred to the operation of another cause. Of this kind are the mixtures, or combinations, of water with oil of vitriol—of alcohol with water—of ether with alcohol—of various oils with each other, &c. In all these cases the bodies seem to unite in all proportions; and therefore to constitute an exception to the definite proportionalism already treated of. However, it is easy to conceive these seemingly exceptional cases of apparent combination in all proportions to result from the intimate mechanical mixture of a limited number of chemical compounds. This hypothesis is well illustrated by a consideration of four remarkable compounds of sulphuric acid and water. The ordinary oil of vitriol, of English commerce, is a definite compound of forty parts by weight of real or dry sulphuric acid, and nine parts by weight of water; and so well combined are the two, so stable is the compound, that, if sufficient heat be applied, the whole evaporates, and may be condensed unchanged as oil of vitriol or common sulphuric acid. There exist, however, three other definite compounds of water and sulphuric acid, the most remarkable of which has the ratio of eighty parts by weight of acid to nine of water, and exists in the German or Nordhausen variety of sulphuric acid. If this variety be gradually heated, pure dry sulphuric acid is evolved, and common oil of vitriol remains behind.

These various combinations of sulphuric acid with water have been studied by Mr. Graham, who arranges them as follows:—

	Parts by weight. Water.		Acid.
Hydrate existing in the German or Nordhausen acid	1	+	2
Oil of vitriol	1	+	1
Acid of sp. gr. 1·780	2	+	1
Acid of sp. gr. 1·632	3	+	1

It is evident, from this consideration, that the hydrates of sulphuric acid furnish well-marked instances of definite proportionality. It is not difficult to conceive that these various hydrates, by mingling indefinitely with each other and with water, may furnish an apparently indefinite aqueous combination. A similar explanation may be applied to the various possible compounds or mixtures of alcohol and water, and all other combinations of the same nature; such as that of acids with water, acids with each other, &c. In a practical sense, these compounds are of great utility, although theoretically considered, they do not present much interest.

The next form of apparent combination to be discussed is that in which bodies unite in all proportions up to a certain point. Thus a hundred parts of water are capable of dissolving any quantity of common salt not exceeding forty parts. At this point the capacity for solution terminates, apparently because the cohesive force of the salt crystals now balances the dissolving force of the fluid. Were the cohesive force not in operation, it is probable that solution would go on in all proportions; under which circumstances examples of this kind would be referred to the former category.

In all cases, involving the apparently indefinite union of bodies with each other, the circumstance will be remarked, that the resulting compound will be a substance possessing qualities in which the original qualities of the bodies entering into combination may be traced, and from which the components may be separated unchanged. Thus a mixture of alcohol and water possesses just those properties which are a mean between the evident properties of alcohol and of water. By one of several processes, the two may be demonstrated to exist in union; may be separated each unchanged, each in its original proportion. The same remark applies to the indefinite, or seemingly indefinite, compounds of alcohol with others of salt and water within the limits prescribed, and generally to all parallel cases. When definite proportionalism comes into operation, a marked concomitant is observable. The compounds then resulting are characterized by acquiring properties different from either of their constituents.

For examples of this first, we might turn at random to any part of chemistry, so fertile is it in phenomena of this kind. The position may, however, be conveniently illustrated by the following cases:—The crystallized salt, sulphate of magnesia (Epsom salt), is a compound of sulphuric acid, water, and magnesia; yet the original properties of all these substances are so veiled as to be unrecognizable in the compound. Gypsum, or sulphate of lime, is a compound of lime, sulphuric acid, and water. It is a substance in which neither the properties of lime nor sulphuric acid, though both are well marked, nor of water, though also well individualized, can be distinguished. Whenever definite proportionalism comes into operation, these metamorphoses of original qualities are effected; without it, never. Hence such combinations must be considered as marking the exercise of powerful chemical affinity, and determining its relations to the other forces.

From the observations which precede, it will appear that the operations of chemical affinity may be classified into the following categories :—

1. Bodies which unite, or appear to unite, in all proportions.

2. Bodies which unite, or appear to unite, in all proportions within certain invariable limits.

3. Bodies which unite in definite proportions only.

Although it be impossible to offer a precise definition, which shall be competent to point out the exact line of demarcation between mechanical admixture and chemical combination, yet probably it might be justifiable to limit the terms *chemical combination* and the *operation of chemical attraction*, to those cases in which the product of combination is not a mere result out of the qualities possessed by each component, but where the original qualities have entirely merged.

Understanding the definition in this sense, then, without any reservation it might be asserted that bodies unite chemically, in proportions fixed and invariable; that the progression of the series being studied, a regular order of numerical progression is manifested, in which the highest numeral term bears some simple relation to the lowest.

Definite Proportionality.—Under all circumstances, whether the definition of affinity be restricted as above suggested, or extended in such a manner as to comprehend the various seemingly indefinite combinations, definite proportionality is a concomitant of every well-marked case of the exercise of affinity; of the operation of which force it is to be regarded as the strongest indication, of its character the most prominent type. It is to a consideration of these definite compounds of substances alone that the remaining portions of this section will be devoted.

For the purpose of deriving some knowledge of the ratios in which simple bodies unite, we may with convenience regard the proportional elements of water as the basis of future remark and comparison. Water, as has been shown, consists of one volume of hydrogen and half a volume of oxygen, united together and condensed; by weight, eight parts of oxygen combined with one part of hydrogen. By substituting chlorine, iodine, and bromine for the oxygen, we get the following series :—

	Parts by weight.	Parts by measure.			Weight of compound.
Water	$O_8 + H_1$	$O_1 + H_2$	or	O: 8, H: 1	= 9.
Hydrochloric acid .	$Cl_{36} + H_1$	$Cl_2 + H_2$	or	Cl: 35, H: 1	= 36.
Hydriodic acid . .	$I_{125} + H_1$	$I_2 + H_2$	or	I: 125, H: 1	= 126.
Hydrobromic acid .	$Br_{80} + H_1$	$Br_2 + H_2$	or	Br: 80, H: 1	= 81.*

From the inspection of this table it will appear, that the ponderable quantity of chlorine necessary to take the place of one part by weight of hydrogen is equal to

* In this and succeeding diagrams fractional numbers will, for the sake of simplicity, be avoided in the numbers indicative of equivalent or atomic weights; the nearest whole number to the accepted atomic weight being chosen.

35; of bromine, 80; and of iodine, 125. Hence the propriety of the terms equivalent, and equivalent number; for if 8 parts by weight of oxygen can take the place of 35 parts of chlorine, 80 parts of bromine, and 125 parts of iodine, then with great propriety may it be said that *eight* is the equivalent number for oxygen, or the number of its combining proportion. The same number is also said to be the *atomic* number for oxygen, 36 the atomic number for chlorine, &c., for reasons which will presently be made apparent.

The numeral proportionality which has been seen to hold good for the binary combinations of hydrogen with oxygen, chlorine, iodine, and bromine, are found to hold good for all other elements; and inasmuch as compounds are the sum of their combined elements, so the equivalent number of a compound is the sum of the equivalent numbers of the elements entering into it. Thus we have seen the equivalent weight of hydrogen to be represented by 1, of oxygen by 8; therefore the equivalent weight of water must be equal to 8 + 1, or 9. Hence the equivalent number of simple bodies being remembered, and their proportions entering into any particular compound, it is easy to ascertain, by a simple operation of addition, what is the equivalent number belonging to the compound.

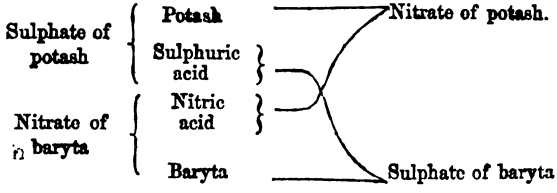
Law of Definite Combination.—It is impossible to overrate the importance of this law of definite combination. To the theoretical chemist it affords an insight into the probable atomic constitution of matter, enabling him to advance on grounds of probability and rational arguments, in a matter concerning which philosophers of antecedent ages have been guided by metaphysical speculations on the one side, and strained mathematical analogies on the other. To the practical chemist it affords a means, no less easy in application than unerring in its results, of learning the necessary quantities of substances to be used in his processes, and anticipating the quality and the quantity of his results.

As an example of the advantages conferred by an acquaintance with the laws of definite chemical proportionalism, I will cite one simple case, although in conducting the description it will be necessary to assume the knowledge of certain facts not yet treated of, concerning which the reader may probably be unacquainted.

It is a quality of sulphuric acid, in whatever soluble form existing, whether simple or in combination, to combine with the earth baryta, and to be precipitated in the form of sulphate of baryta—a most insoluble compound.

First, let the simple case be assumed that a certain liquid—perhaps water—contains a certain but small amount of sulphuric acid, which amount it is desired, by way of analysis, to separate. To evaporate away the water and leave the sulphuric acid, in the condition of one part acid to one of water (oil of vitriol of commerce), if possible at all, would at any rate be exceedingly difficult, and would involve the necessity of an amount of delicacy in manipulation far too great for ordinary practice. Having confidence, however, in the law of chemical proportionality, and being aware that the combination of sulphuric acid with baryta is an insoluble body, the operator would proceed to throw in some of a solution containing baryta—nitrate of baryta for example—and he would continue the operation so long as any precipitate made its appearance; he would then dry his precipitate, weigh it, and referring to some list of chemical equivalents, for the purpose of ascertaining the proportional combination of sulphuric acid with baryta, would find that every 116 parts of sulphate of baryta contained forty parts of sulphuric acid. On this principle of indirect demonstration are by far the greater number of analytical points determined.

Extending the sphere of our observation, let it be assumed that a manufacturer, having a given weight of nitrate of baryta in solution, desires to form nitrate of potash and sulphate of baryta, by the addition of sulphate of potash, a decomposition which may be thus represented by means of a diagram.

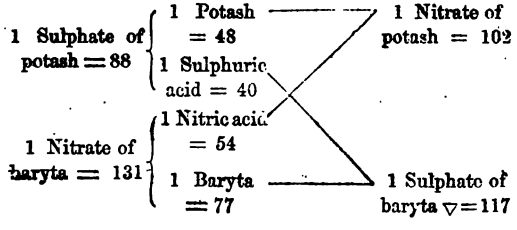


In this diagram the qualitative decomposition is represented, no cognizance being taken of quantities. The diagram is so arranged that the nitrate of potash, remaining in solution, appears in the upper part, whilst sulphate of baryta, being insoluble, precipitates, as very conveniently indicated by a triangle, with its apex downwards.

The measure of information given by this diagram is extremely slight, compared with what it would have been had the proportional quantities of substances entering into decomposition been indicated. The diagram shall, therefore, be reconstructed, so as to embody the following facts :—

The equivalent or combining number of sulphuric acid is . .	40
" " " of baryta . . .	77
" " " of nitric acid . . .	54
" " " of potash . . .	48
Sulphate of baryta is composed of 1 equivalent baryta + 1 equivalent of sulphuric acid; its equivalent number is, therefore	117
Nitrate of potash is composed of 1 equivalent of nitric acid + 1 equivalent of potash; therefore its equivalent number is	102

Reducing this fact to a diagrammatic form, we have—



Thus it would appear that, supposing 131 parts of nitrate of baryta to be in solution, eighty-eight parts of sulphate of potash would be required for its complete decomposition. The result would be 117 parts of sulphate of baryta, and 102 parts of nitrate of potash. It need scarcely be indicated that the ratio of combination

being once known, the quantity of nitrate of potash and sulphate of baryta for any possible quantities of sulphate of potash and nitrate of baryta may be ascertained by a simple rule of proportion.

An examination of the preceding diagram will afford a ready explanation to a circumstance first noticed by the Saxon chemist, Wenzel—that when two neutral salts decompose each other, the results are also neutral, because if bodies combine in the ratio of their equivalents, it is evident that the mutually exchanging bodies, being mutual equivalents, possess a mutual satisfying power. This expression of an isolated fact would, if extended to other facts of parallel character, and reasoned upon, have led to a knowledge of the universality of definite proportionalism.

There are many examples in which bodies unite in one proportion only; and in all such cases the proportion of the elements of a compound must be uniform for the species. Thus, hydrogen and chlorine unite in no other proportions than those constituting hydrochloric acid, which, by weight, are one of the former to thirty-five of the latter. Whatever of either ingredient is in excess remains uncombined after the experiment. In cases of this sort, combination is generally energetic, and the characteristic qualities of the components are no longer observable in the compound.

Other bodies unite in several proportions; but these proportions are definite, and, in the intermediate ones, no combination ensues. Thus six parts by weight of carbon combine with eight of oxygen, or with sixteen, but with no intermediate quantity; sixty-four parts of copper combine with eight of oxygen, or with sixteen, and with those proportions only. This law of *combination in definite proportions*, though deducible from the previous experiments of Wenzel, seems to have been first discovered and established by a series of researches undertaken with that view by Richter of Berlin, and published between the years 1796 and 1798. The great object of that chemist was to determine the relative capacity of saturation of the acids and bases, and to represent them by a series of numbers, serving the same purpose as the Tables of Chemical Equivalents now constructed. It is unnecessary to copy the Table of Richter, because the results are, for the most part, inaccurate; but, notwithstanding this, the merit of the first conception of such a table unquestionably belongs to him. Prout afterwards contributed to establish the law, by showing that iron and antimony do not unite with oxygen in all proportions, but only in very few determinate ones; and, in a controversy with Berthollet, which was most ably and temperately conducted on both sides, he urged convincing arguments in favour of limited combinations.

It now remains to investigate the ratios which subsist in series of combinations. These ratios are exceedingly simple, being one of the following series. Either

A unites with 1, 2, 3, 4, 5, &c., of B; or,
A unites with 1, $1\frac{1}{2}$, 2, $2\frac{1}{2}$, 3, $3\frac{1}{2}$, &c., of P.

The first series comprehends by far the larger number of chemical combinations. One example has already been furnished by the series of water and peroxide of hydrogen. Thus

	Parts by weight. Hydrogen.		Oxygen.	Ratio.
Water	1	+	8	1
Peroxide of hydrogen	1	+	16	2

The two oxygen compounds of carbon also afford an examplification.

	Parts by weight. Carbon.		Oxygen.	Ratio.
Carbonic oxide	6	+	8	1
Carbonic acid	6	+	16	2

A more extended series is furnished by the nitrogen compounds with oxygen, which interesting for the further reason that this series was the one first cited by the illus- ous Dalton, as exemplifying his theory of atoms, soon to be discussed.

	Parts by weight. Nitrogen.		Oxygen.	Ratio.
Protoxide of Nitrogen . . .	14	+	8	1
Binoxide of Nitrogen . . .	14	+	16	2
Hyponitrous acid	14	+	24	3
Nitrous acid	14	+	32	4
Nitric acid	14	+	40	5

Compounds belonging to the second series are more rare. The following are mples: —

	Parts by weight. Iron.	Oxygen.	Ratio.
Protoxide of iron	28	8	1
Sesquioxide	28	12	$1\frac{1}{2}$
Protoxide of lead	104	8	1
Sesquioxide	104	12	$1\frac{1}{2}$
Binoxide	104	16	2
Arsenious acid	38	12	$1\frac{1}{2}$
Arsenic acid	38	20	$2\frac{1}{2}$
Hypophosphorus acid . . .	16	4	$\frac{1}{2}$
Phosphorus acid	16	12	$1\frac{1}{2}$
Phosphoric acid	16	20	$2\frac{1}{2}$

It will be seen, therefore, that not only in all marked cases of chemical combinations substances unite in very simple ratios, but that these ratios of combination for the ie bodies are invariable, and that their numeral exponents are mutually propor- ial. An example has been cited of the utility derivable, both to theoretical and to ctical chemistry, from an application of this knowledge, which may be rendered l more readily available by means of the sliding scale of the late Dr. Wollaston. iiling himself of the well-known properties of a logarithmic scale of numbers, this losopher subjected the numbers of chemical equivalents to this arrangement, by ich the resulting proportions of any elements, as also the proportions of new sub- nces generated from their action, can be read off by simple inspection.

As a slight inspection of this instrument renders evident its principles and its appli- ion, further description is unnecessary. Its employment, however, cannot be too ngly recommended to all who have much occasion for calculating the amounts of cting substances, and the products generated.

It is to Dr. Dalton that we are indebted for the first correct instance of such a ple multiple in the union of nitrous gas with oxygen, and for the first distinct icipation, founded on well-ascertained facts, of the general law of multiple com-

bination. For, though it is due to the late Mr. Higgins, of Dublin, to state that, in an ingenious work, published in 1789, entitled, "A Comparative View of the Phlogistic and Antiphlogistic Theories," he had represented the combinations of azote with oxygen, and those of sulphur with oxygen, to form such a series that the successive doses of oxygen are all equal multiples of the first; yet, as Dr. Wollaston has remarked, "these proportions were conceived, rather than observed, to occur." Little attention seems, indeed, to have been given to the subject until the year 1808, when facts of a similar kind, but under a more tangible form, were published by Dr. Thomson and Dr. Wollaston, with regard to neutral and superacid, or subacid, salts. These facts all tended to show that the quantity of acid, combined with bases in certain super-salts, is precisely double; and in certain sub-salts, precisely half, of that which is saturated by the same quantity of base in their neutral compounds.

Law of Volumes.—An extension of the law of definite proportions, so far as respects aëriform bodies, has been proposed by Gay Lussac, namely, that they combine in proportions determinable by *volume*, the ratios being 1 *volume* of A to 1 of B, or 1 to 2, or 1 to 3, &c. Water, for example, results from the union of two volumes of hydrogen gas with one volume of oxygen gas; hydrochlorate of ammonia from one volume of muriatic acid gas + 1 of ammonia; nitrous gas from one measure of oxygen + 1 of nitrogen; nitrous oxide from 1 oxygen + 2 nitrogen; nitrous acid from 2 oxygen + 1 nitrogen.

When the product remains gaseous, there is either no condensation of elements, or, if there be a condensation, it bears some simple and uniform relation to the volumes of the gases which have combined: Thus,

Vol.		Vol.		Vol.
1 of chlorine	+	1 hydrog.	=	2 hydrochloric acid gas.
2 of hydrog.	+	1 oxyg.	=	2 aqueous vapour.
1 of nitrog.	+	½ oxyg.	=	1 nitrous oxide.
1 of nitrog.	+	1 oxyg.	=	2 nitrous gas.

Having established the law of definite and multiple volumes, in a variety of cases admitting of the actual measurement of the volumes before and after combination, Gay Lussac extended it to other cases of chemical union, where one of the bodies is not known to us as a gas in its separate form. For example, we have never yet seen gaseous carbon; but we conclude from analogy that, at a sufficiently high temperature, it would be capable of being volatilized. We know, also, that by combination with oxygen and with hydrogen, carbon furnishes gaseous compounds, and that oxygen gas, by having charcoal burned in it, has its specific gravity increased from 1·1111 to 1·5277, its volume remaining the same. The difference between these two numbers will, therefore, denote the weight of carbon which a volume of oxygen has absorbed—viz., 1·5277 − 1·1111 = 0·4166. From analogy, Gay Lussac concludes, that one volume of gaseous carbon unites with one volume of oxygen gas to form carbonic acid, and that 0·4166 represents the weight of the former. But it is evident that the facts are equally well explained, if we suppose a greater or less volume of gaseous carbon to be so combined, provided its weight be proportional; for example, two volumes of carbon weighing half the above number, or 0·2083 × 2, may unite with one volume of oxygen to form carbonic acid. In all such instances, then, it is matter of theory that bodies, not known to us as gases, unite in volumes which are equal, or multiples, or

sub-multiples, of those of known gases; nor can we be certain, admitting the probability of such combinations, that the volumes assigned are actually the true ones.

Of the Atomic Theory.—The remarkable proportional relation existing between substances entering into chemical combination, manifesting itself not only in weight but in volume also, so far as our cognizance of volume can penetrate, can scarcely be observed without arousing speculations as to the cause of such proportionality. No *à priori* reason could have been offered why eight and sixteen parts, by weight, of oxygen respectively, should combine with one part by weight of hydrogen; but in no intermediate proportions. Neither could any *à priori* reasoning be adduced to explain why the eight parts by weight of oxygen gas should occupy exactly twice the space of one part by weight of hydrogen. But such being the laws of their combination, the law of proportional volumes extending to all substances which have hitherto been examined in the state of gas or vapour, and the law of proportional weights being universal for all classes of bodies,—whether solids, liquids, or gases,—facts so curious in themselves, so important in their applications, might naturally create a desire to comprehend their rationale.

Turning his mind in the channel of these speculations, it occurred to the sagacity of the illustrious Dalton, that the definite proportionality of chemical combination could most naturally be accounted for on the assumption of the atomic constitution of matter. Thus originated the modern atomic theory, which, for beauty and comprehensiveness, is probably not excelled by any other speculation; whether in chemistry or in any other science.

Before offering any remarks on the bearing which definite proportionality has on the theory of atoms, it may be desirable to present a sketch of the progress of this theory, from ancient times to the present. First, then, what are we to understand by the term, atom? Popular appreciation associates the word atom with an idea of some exceedingly small particle, an idea which is practically correct. This idea, however, fails to convey the most characteristic quality of an atom, a term immediately derivable from the Greek words *a* ταμων—*i. e.*, incapable of being cut, or indivisible.

In order to have a correct appreciation of atoms, it does not suffice to regard them as very small particles of matter. This is an idea secondary in its nature, collateral to the subject,—not bearing directly upon its chemical character. The direct idea is that of indivisibility. Any portion of matter which cannot be further divided is, according to the definition, an atom, irrespective of the area in space which it may fill. Inasmuch, however, as the most ordinarily occurring phenomena show that matter of whatever kind can be divided indefinitely, within any limits of which our senses can take cognizance—therefore, supposing matter to be atomic, it follows that such atoms must be exceedingly small. Hence the indirect or oblique idea of smallness which has come to attach to the expression, atom. A keen controversy was carried on amongst the ancient Greeks as to atomic or non-atomic division of matter. According to one side, it was assumed that matter could be divided indefinitely; according to the other, it was assumed that, on carrying subdivision to a certain extent, a limit would at length be arrived at, beyond which matter was no longer divisible. This argument was carried on with great pertinacity, and supported with plausible evidence, on either side; but followed by no practical result.

In opposition to the existence of atoms, it was argued to be irrational to suppose that any particle of matter, however small, might not be further divided. In favour

of their existence, the counter-argument was advanced, that the non-atomists had introduced into their reasonings the fallacy of confounding matter with the space it occupies; that although space may be conceived to be infinitely divisible, yet matter filling space may, nevertheless, be composed of particles so hard that no existing power can sever them,—which postulate granted, matter would necessarily be atomic.

Thus the question rested until the discovery of lenses created a new hope that atoms, if they really existed, might be seen; but all attempts of this kind having proved fruitless, the dispute was, by tacit consent of philosophers, allowed to rest, as being amongst those impenetrable subjects which, admitting of no proof, only furnish a scope for the exercise of sophistry, and the wanderings of mysticism. But when the law of *definite proportions* and that of *multiple proportions* had been established by a sufficient number of examples, it became natural to inquire what is the reason of this uniformity, and what is the cause which renders combination in other proportions impossible. Mr. Higgins, taking for granted the correctness of the instances already quoted, had been led to conceive the theory of combination by ultimate particles, and to illustrate it by a series of diagrams, so constructed as to explain the phenomena of chemical decomposition by a comparison of the attractive forces of those particles. But, though there is much in Mr. Higgins's views that entitles him to the praise of great ingenuity, yet they are, in several respects, erroneous, and are at best to be considered as mere hints, which were not subjected by their author, at any subsequent period, to a more copious and rigorous induction, nor indeed estimated by him, at the time, as of the importance which really belonged to them.

A few years afterwards, Dr. Dalton, without the slightest knowledge of the previous speculations of Mr. Higgins, formed the first distinct conception of that happy generalization, which now passes under the name of the *Atomic Theory of the Chemical Constitution of Bodies.* To this he was led by long and patient reflection on the then ascertained phenomena of chemistry. In October, 1803, he communicated to the Manchester Society an essay, containing the first general outline that was published of his speculations.* This was followed, in 1808, by a fuller, but still very concise, development of his views, in the first part of his "New System of Chemical Philosophy." Of this theory such illustrations as are now offered will render it intelligible to the reader.

When the chemical union of bodies is effected, though it appears to operate on *masses*, yet it is consistent with the most rational view of the constitution of bodies to believe that it is only between their *ultimate particles* that combination takes place. Of such ultimate particles the existence, it must be confessed, cannot be demonstrated; nor can anything more than a high degree of probability be alleged in favour of their existence; this degree of probability, however, much outweighs any that can be produced in proof of the infinite divisibility of matter. On this subject the immortal Newton, after reflecting on the then known chemical phenomena, has thus expressed himself (in the thirty-first Query, subjoined to his Treatise on Optics, fourth edition, p. 350):—"It seems to me probable that God, in the beginning, formed matter in solid, massy, hard, impenetrable, moveable particles, of such sizes and figures, and with such other properties, and in such proportions to space, as most conduced to the end for which he formed them; and that the primitive particles, being solids, are incomparably harder than any porous bodies compounded of them; even so very hard, as never to wear or break in pieces,

* Man. Mem. Second Series, vol. i. 286. To this Essay Dr. Dalton has annexed "A Table of the Relative Weights of the Ultimate Particles of Gaseous and other Bodies."

no ordinary power being able to divide what God himself made one in the first creation," &c. To this argument, drawn from general physics, others of a similar kind have been added by Leibnitz and Boscovich; and conclusions, of the same tendency, have, in more recent times, been deduced from astronomical observations. In an essay on the Finite Extent of the Atmosphere, published in the Phil. Trans. for 1822, Dr. Wollaston has observed, that "since the law of definite proportions, discovered by chemists, is the same for all kinds of matter, whether solid, fluid, or elastic, if it can be ascertained that any one kind of matter consists of particles no longer divisible, we can then scarcely doubt that all other bodies are similarly constituted; and we may without hesitation conclude that those equivalent quantities, which we have learned to appreciate by proportionate numbers, do really express the relative weights of elementary atoms, the ultimate objects of chemical research." From a series of observations on the planet Jupiter, Dr. Wollaston was led to conclude, that "as this planet has not his due share of an infinitely divisible atmosphere, the universal prevalence of such a medium cannot be maintained; while, on the contrary, all the phenomena entirely accord with the supposition that the earth's atmosphere is of finite extent, limited by the weight of ultimate atoms of definite magnitude, no longer divisible by repulsion of their parts."

The ultimate particles, then, or atoms, of all bodies, probably consist of solid corpuscles, each of which forms a nucleus, surrounded by an atmosphere of heat. Absolute contact is not supposed ever to take place between the atoms even of inelastic bodies, since, at all temperatures to which we have access, the subtraction of heat from a body is followed, except when the body changes, or is about to change its state, by a contraction of volume. Of simple atoms, it seems most probable that the *shape* or *figure* is spherical. But, of compound atoms, consisting of a single central atom, surrounded by other atoms of a different kind, it is obvious that the figures (contemplating the solid corpuscles only) cannot be spherical; yet, if we include the atmosphere of heat, the figure of a compound atom may be spherical, or some shape approaching to a sphere.

Taking for granted that combination takes place between the atoms of bodies only, Dr. Dalton has deduced, from the *relative* weights in which bodies unite, the *relative* weights of their ultimate particles, or atoms. This is all that we are likely to determine respecting them; for it is not probable that our knowledge will ever extend beyond the *ratios* of these weights. When only one combination of any two elementary bodies exists, he assumes, unless the contrary can be proved, that its elements are united atom to atom singly. Combinations of this sort he calls *binary*. But, if several compounds can be obtained from the same elements, they combine, he supposes, in proportions expressed by some simple multiple of the number of atoms. The following table exhibits a view of some of these combinations:—

1 atom of A + 1 atom of B = 1 atom of C, binary.
1 atom of A + 2 atoms of B = 1 atom of D, ternary.
2 atoms of A + 1 atom of B = 1 atom of E, ternary.
1 atom of A + 3 atoms of B = 1 atom of F, quaternary.
3 atoms of A + 1 atom of B = 1 atom of G, quaternary.

These combinations Dr. Dalton represented by characters, of which, as they have not come into general use, I shall offer only a few examples. From their figure, they appear to me better adapted than symbols of any other shape, to aid our conceptions of

the manner in which spherical atoms may unite. Oxygen is denoted by ○; Hydrogen by ⊙; Nitrogen by ⦶; Carbon by ●; and so of the rest.

In water we have 1 atom of oxygen united with 1 atom of hydrogen, ○ ⊙. The binary compound of oxygen and nitrogen may be represented by ○ ⦶. The ternary compound by ○ ⦶ ○. The quaternary compound by $\overset{\bigcirc}{\underset{\bigcirc}{⦶}}\bigcirc$.

As an illustration of the mode in which the relative weights of the atoms of bodies are determined, let us suppose that any two elementary substances, A and B, form a binary compound; and that they have been proved experimentally to unite in the proportion, by weight, of 5 of the former to 4 of the latter; then since, according to the hypothesis, they unite particle to particle, those numbers will express the relative weights of their atoms. But besides combining atom to atom singly, 1 atom of A may combine with 2 of B, or with 3, 4, &c. Or 1 atom of B may unite with 2 of A, or 3, 4, &c. When such a series of compounds exist, the relative proportion of their elements ought necessarily, on analysis, to be proved to be 5 of A to 4 of B; or 5 to (4 × 2 =) 8; or 5 to (4 × 3 =) 12, &c.; or contrariwise, 4 of B to 5 of A; or 4 to (5 × 2 =) 10; or 4 to (5 × 3 =) 15. Between these there ought to be no intermediate compounds: and the existence of any such (as 5 of A to 6 of B, or 4 of B to 7½ of A) would, if clearly established, militate against the hypothesis.

To verify these numbers, it is necessary to examine the combinations of A and B with other bodies. Let us take C for example; and let us suppose that A and C form a binary compound, in which analysis discovers 5 parts of A and 3 of C. Then, if C and B are also capable of forming a binary compound, the relative proportion of its elements ought to be 4 of B to 3 of C; for these numbers denote the relative weights of their atoms. Now this is precisely the method by which Mr. Dalton deduced the relative weights of oxygen, hydrogen, and nitrogen; the two first from the known composition of water, and the two last from the proportion of the elements of ammonia. Extending the comparison to a variety of other bodies, he obtained a scale of the relative weights of their atoms; which, corrected to agree with recent experiments, is as follows:—

1. In *water*, the hydrogen is to the oxygen as 1 to 8.
2. In *olefiant gas*, the hydrogen is to the carbon as 1 to 6.
3. In *carbonic oxide*, the oxygen is to the carbon as 8 to 6.

Whether, therefore, we determine the weight of the atom of carbon, from the proportion in which it combines with hydrogen, or with oxygen, we arrive at the same number, 6: an agreement which, as it occurs in various other instances, can scarcely be an accidental coincidence. In a similar manner, 8 is deducible, as representing the atom of oxygen, both from the combination of that base with hydrogen and with carbon; and 1 is inferred to be the relative weight of the atom of hydrogen from the two principal compounds into which it enters.

In selecting the body which should be assumed as unity, Dr. Dalton has been induced to fix on hydrogen, because it is that body which unites with others in the smallest proportion by weight. Thus, in water, we have 1 of hydrogen by weight to 8 of oxygen; in olefiant gas, 1 of hydrogen to 6 of carbon; and in sulphureted hydrogen, 1 of hydrogen to 16 of sulphur. Taking for granted that all these bodies are binary compounds, we have the following scale of numbers, expressive of the relative weights of the atoms of their elements:—

Hydrogen	1
Oxygen	8
Carbon	6
Sulphur	16

Drs. Wollaston and Thomson, and Professor Berzelius, on the other hand, have assumed oxygen as the decimal unit (the first making it 10, the second 1, and the third 100), chiefly with a view to facilitate the representation of the numerous compounds of oxygen with other bodies. This is to be regretted, even though the change may be in some respects for the better, because it is extremely desirable that chemical writers should employ a standard of comparison for the weights of the atoms of bodies that may be universally and at once understood; and the hydrogen scale appears to deserve a preference, because the numbers composing it, so far as experiment has yet shown, are so nearly simple multiples of the weight of hydrogen taken as 1, that the deviations from strict conformity to the rule may be safely ascribed to unavoidable errors of manipulation. But the scale, in which oxygen is taken as unity, necessarily involves the use of fractional numbers, as in the following examples:—

	Oxygen = 1.	Oxygen = 10.
Hydrogen	0·125	1·25
Carbon	0·75	7·50
Nitrogen	1·75	17·5

It is true that these numbers are easily converted into each other by a simple arithmetical rule. Thus to know what number would be equivalent (oxygen being supposed 1, 10, or 100) to any known number on the hydrogen scale, say as 8 is to 1, 10, or 100, so is the known equivalent to the number sought. And, on the other hand, the equivalent in the hydrogen series to any known number on the oxygen scale is obtained by the proportion 1, 10, or 100 : 8 : : the given number : the number sought.

When any two bodies unite, so far as we know, in one proportion only, the relative weight of their atoms is in most cases determined by their combining proportion. Thus since hydrogen and chlorine unite only in the proportion by weight of 1 of the former to 35 of the latter, we consider the relative weight of the atom of hydrogen to that of the atom of chlorine to be as 1 to 35. But when one body unites, in different proportions, with another, it is necessary, in order to ascertain the weight of its atom, that we should know the smallest proportion in which the former combines with the latter. Thus, if we have a body A, 100 parts of which by weight combine with not less than 32 of oxygen, the relative weight of its atom will be to that of oxygen as 100 to 32; or, reducing these numbers to their lowest terms, as 25 to 8; and the number 25 will express the relative weight of the atom of A. But if, in the progress of science, it should be found, that 100 parts of A are capable of uniting with 16 parts of oxygen, then the relative weight of the atom of A must be doubled, for as 100 is to 16, so is 50 to 8. This example will serve to explain the changes, that have been sometimes made, in the weights of the atoms of certain bodies; changes which, it may be observed, always consist either in a multiplication, or division, of the original weight, by some simple number. It is proper, however, to state that the combining proportions are not of themselves sufficient, for reasons which will soon be assigned, to decide, in all cases, the true atomic weights of bodies.

In cases where we have the apparent anomaly of 1 atom of one substance united with $1\frac{1}{2}$ of another, it has been proposed by Dr. Thomson (Ann. of Phil. v. 187) to remove the difficulty by assuming that, in such compounds, we have two atoms of the one combined with 3 atoms of the other. This saves us the necessity of speaking of fractions of atoms, which, from the definition of the word *atom*, implying indivisibility, is evidently a contradiction in terms. Such combinations, it is true, are exceptions to a law deduced by Berzelius—*that, in all inorganic compounds, one of the constituents is in the state of a single atom.* But they are in no respect inconsistent with the views of Dr. Dalton; and are, indeed, expressly admitted by him to be compatible with his hypothesis, as well as confirmed by experience. (Ann. of Phil. iii. 174.)

The investigation of the *number of atoms* in compounds is attended with considerable difficulty, and cannot always be decided by the combining proportions merely, without regard to other considerations. On this subject Dr. Dalton, in the second part of his New System, recently published, has made the following remarks:—"When two bodies, A and B, combine in multiple proportions; for instance, when 10 parts of A combine with 7 of B to form one compound, and with 14 to form another, we are directed by some authors to take the smallest combining proportion of one body, as representative of the elementary particle or atom of that body. Now it must be obvious to any one of common reflection, that such a rule will be more frequently wrong than right. For, by the above rule, we must consider the first of the combinations (10 A + 7 B) as containing 1 atom of B, and the second (10 A + 14 B) as containing 2 atoms of B, with 1 atom or more of A; whereas it is equally probable, by the same rule, that the compounds may be 2 atoms of A to 1 atom of B, and 1 atom of A to 1 of B respectively. For the proportions being 10 A to 7 B (or, which is the same ratio, 20 A to 14 B), and 10 A to 14 B, it is clear by the rule, that when the numbers are thus stated, we must consider the former combination as composed of 2 atoms of A, and the latter of 1 atom of A, united to one or more of B. Thus there would be an equal chance for right or wrong. But it is possible that 10 of A and 7 of B may correspond to 1 atom of A and 2 atoms of B; and then 10 of A and 14 of B must represent 1 atom of A and 4 atoms of B. Thus, it appears, the rule will be more frequently wrong than right."

A particular example may, perhaps, render the difficulty above stated more intelligible to the student. Two oxides of copper have been ascertained to exist:

1st. 8 oxygen + 64 copper = the red oxide.
2nd. 16 oxygen + 64 copper = the black oxide.

Now these oxides may be variously contemplated: for we may either consider the first as the true binary compound of 1 atom of oxygen + 1 atom of metal, and the second of 2 atoms of oxygen + 1 atom of metal; or we may (with equal probability, apart from other considerations) view the second as the binary compound of 1 atom of oxygen (8) + 1 atom of copper (32), which are the same proportions as 16 to 64. The first compound will, in that case, come to be regarded as 1 atom of oxygen + 2 atoms of metal, $32 \times 2 = 64$. The latter view, in fact, is the one actually taken of these oxides by Dr. Thomson, who regards the first compound as a suboxide, and the second not, as it is generally considered, as a deutoxide, but as a protoxide. In all cases of this sort, it is necessary to examine, not only the compound of the two elementary bodies with each other, but the compounds of each with other bodies; and also to

balance the probabilities derived from other considerations, such as the comparative facilities with which the respective compounds are formed or decomposed; their convertibility into each other; and the permanence or instability which belongs to them.

When only one compound of any two *gaseous* elements, A and B, exists, it is most reasonable to suppose that it is composed of 1 atom of A + 1 atom of B, because an additional atom of either element (B for example) would introduce a new force, diminishing the attraction of the two elements for each other, viz. the mutual repulsion of the atoms of B; and this repulsion will be the greater, in proportion as we increase the number of the atoms of B. When more than one compound of two elements, A and B, exists, that which is with most difficulty decomposed is probably the binary one of atom to atom. For example, it is much more probable that water is constituted of an atom of oxygen + an atom of hydrogen, than that the peroxide of hydrogen should be so composed; for in the latter, one proportion of oxygen is so weakly combined as to escape merely by virtue of its own elasticity.

The difficulty of deciding upon the actual number of atoms, which, on the assumption of the atomic theory, any particular compound of a series should possess, can be still further illustrated by contemplating the law of combination by volume. Thus water, as we have seen, is a compound of two volumes hydrogen with one volume oxygen.

= Water.

= Peroxide of hydrogen.

And binoxide, or peroxide of hydrogen, is a compound of equal volumes. How are we to arrive, from the consideration of data here given, at a knowledge of the true atomic constitution of these two substances? Two suppositions are possible. Either the atomic volume of oxygen is half that of hydrogen, and water is a compound of an equivalent of each, or it may also be assumed that the atoms of oxygen and hydrogen fill equal spaces; in accordance with which supposition water would be a compound of one of oxygen and two of hydrogen, and the peroxide of hydrogen would be composed of two equivalents of each of its constituents; in either case the ratio of composition remaining the same. Accordingly, many continental chemists, following the example first set by Berzelius, believe in the equal size of all atoms, when compared in the same cohesive state, and thus regard water as not a protoxide of hydrogen, but a suboxide.

This theory has never been much adopted by British chemists; and, indeed, its assumption involves such a complexity of relations with other compounds as to render its adoption most inconvenient in practice, even if the balance of theoretical arguments were in its favour. The balance of theoretical arguments is, however, against it.

Hence, it cannot fail to be recognised, that however correctly the ratio of combination may have been determined for a series of bodies, still the numeral basis of this ratio, on the determination of which depend our ideas concerning the number of atoms, remains a pure matter of speculation. Thus we know as a fact, that peroxide of hydrogen contains twice the quantity, by weight and by volume, of oxygen that water contains; but whether the series of two is to be regarded in accordance with

the first or the second of the appended schemes, a mere knowledge of their combining ratios cannot alone further aid us to determine.

THEORY OF DALTON, (Usually accepted in England).					THEORY OF BERZELIUS.				
	By weight.		Atoms.			By weight.		Atoms.	
	H.	O.	H.	O.		H.	O.	H.	O.
Water	1	8	1	1	Water	1	8	2	1
Peroxide of hydrogen	1	16	1	2	Peroxide of hydrogen	1	16	2	2

It seems rational to assume, however, that the most permanent compound of a series should be that generated by the combination of equal atoms. Now water is a remarkably permanent compound. It is the only compound of oxygen and hydrogen found in nature. It is the phase of combination into which oxygen and hydrogen are prone to assume. On the other hand, peroxide of hydrogen may be designated as a strained or forced compound, never occurring in nature, brought into operation by an indirect chemical process, its particles held together by overstrained forces, and half its oxygen prone to be evolved by very slight causes, leaving water as the fixed result. These facts being considered, it seems most rational to assume that water is the real protoxide of hydrogen—the real combination of single atoms. Another power by which it has been proposed to determine the compound of single atoms in a binary series, is that of voltaic electricity. Davy believed that all compounds should be capable of decomposition by electricity, supposing that the amount of electricity applied were sufficiently great. Faraday, however, has demonstrated, that out of any series of binary compounds, only one is capable of direct decomposition by electricity. Collateral reasoning has led this philosopher to the belief that the particular compound of any series, thus subject to electrical decomposition, is the one which is a direct combination of atom to atom. The doctrine being accepted, the proof of monatomism would be capability of electric decomposition—a strong presumptive argument in favour of the supposition that the compound so decomposed possessed a single atomic constitution.

A third means of arriving at the determination of the number of atoms contained by a compound is suggested by a curious deduction, first made by Messrs. Petit and Dulong (Ann. de Ch. et Phys. vol. x. 403), and since followed out by M. Regnault.

According to the results of these experiments, it would seem highly probable that the atoms of all simple substances—that is, their equivalent weights—have all the same capacity for heat. Hence, the specific heat of any simple substance, multiplied by its equivalent number, should yield a constant quantity. Subjecting to this operation the accepted atomic weights of simple bodies, it is found that most of them really comply with the theoretical conditions; the product of their atomic weight and specific heat is a fixed number. But certain elements vary from this rule; and in such cases the ratio of variation is measured by some multiple or sub-multiple of the accepted atomic number. Thus, for instance, it has been found that carbon, when its atomic or equivalent number is multiplied into the number expressing its specific heat, does not yield the theoretical product, but exactly half that product; hence, supposing the theory of M. M. Petit and Dulong, and Gay Lussac, to be accepted, the combining proportion of carbon should be double that we usually accept—that is to say, it should be 12 instead of 6.

When discussing the subject of heat, the above speculations will be further treated of in detail. They have been merely adverted to in this place for the purpose of show-

ing one means proposed for determining the number of atoms entering into a binary compound.

In every science it is necessary clearly to distinguish between what is certain and what is merely probable. The laws of combination, in definite and multiple proportions, appear to belong to the former class; but the generalization, which explains these truths by speculations respecting atoms, must be acknowledged, in its present state, to be entirely theoretical. The probabilities, however, in favour of this theory increase with the progress of science. That bodies consist of ultimate indivisible atoms—that these ultimate atoms have in different bodies different weights—that it is only between these atoms that chemical combination takes place—and then either between single atoms, or by simple multiples of atoms—are propositions which may be considered as safe ground for our future reasonings. But the details of the theory, it must be acknowledged, are still open to further investigation, and no one was more aware than the illustrious author of it himself, that we still want data sufficiently exact for determining the relative weights of the atoms of many bodies, especially of those which are known to us only in a gaseous state. (See his New System, vol. ii. p. 351.) No better service could be rendered to chemical science than the accurate determination of these most important data, which ought not to rest on the testimony of any one individual, however great his reputation or his skill, but to be decided by the concurrent testimony of witnesses competent to the task, and uninfluenced by theoretical predilections.

Although hydrogen be adopted as the unit of proportional relation, the adoption is one of mere convenience, and totally irrespective of a theory first advanced by Dr. Prout, and propounded on the evidence of experimental demonstration by Dr. Thomson. By this theory the atomic weights of all bodies were assumed to be multiples of the atomic weight of hydrogen by a whole number. If this doctrine were established, then a table of equivalent weights—hydrogen being unity—should, theoretically speaking, contain no fractions; and, practically, any fractions thus appearing should be referable to errors of calculation.

This doctrine was strenuously opposed by Berzelius, as being inconsistent with his deductions; and the late Dr. E. Turner having gone through the experiments necessary to determine the matter at issue, gave his adhesion to the views of the Swedish chemist. Accordingly, in the table of atomic or equivalent numbers, which will be found under the head of Chemistry of the Ponderable Agents, fractional parts will be given.

On the law of volumes, as first generalized by M. Gay Lussac, were founded some interesting speculations, published anonymously in Dr. Thomson's Annals of Philosophy, for Nov. 1815, but since acknowledged by Dr. Prout, *On the Relation between the Specific Gravities of Bodies in their Gaseous State, and the Weight of their Atoms.* Assuming atmospheric air to be constituted of four volumes of azote, and one volume of oxygen, and considering the weight of the atom of oxygen as 10, and that of the atom of azote as 17·5, he finds the specific gravities to be

Of oxygen gas	1·1111
Of azote	·972

From the specific gravity and composition of ammonia he deduces the specific gravity of hydrogen gas to be 0·0694. The specific gravity of oxygen thus obtained is, therefore, exactly 16 times that of hydrogen, and the specific gravity of azote just 14 times. By a similar method he inferred the specific gravity of other gases, and also

of some elementary substances in a gaseous state, that do not at ordinary temperatures exist in that state; and he embodied the results in the form of tables, from which he drew the then remarkable conclusion, that *all the elementary numbers, hydrogen being considered as* 1, *are multiples of the atomic weight of hydrogen by a whole number.* Dr. Prout also first pointed out that to find the specific gravity of any substance in the state of gas, we have only to multiply half the specific gravity of oxygen gas by the atomic weight of the substance, with respect to oxygen. For instance, the combining ratio in volume between oxygen and iodine is as $\frac{1}{2}$ to 1, and the combining ratio in weight as 1 to 15·5. Now ·5555, the density of half a volume of oxygen, multiplied by 15·5, gives 8·61111 for the specific gravity of vaporous iodine. In several instances, the numbers thus deduced have been confirmed by a valuable series of experiments, undertaken by Dumas, with the view of determining the atomic weights of bodies by the density of their vapours. (Ann. de Chim. et de Phys., Dec. 1826.) The specific gravity of gaseous iodine, for example, Dumas finds by experiment to be 8·716, a deviation from the theoretical number (8·6111) of too small amount to impeach the accuracy of the method of reasoning, from which the latter number had been derived.

The definite proportionality of chemical compounds, which imparts such weight to the arguments in favour of the atomic constitution of bodies, admits, however, of another explanation. Instead of being due to the limitation of size and weight of combining atoms, it may be due to mere limitations of combining force.

With respect to this matter, a train of very beautiful speculations has been entered upon by M. Dumas, who has drawn the attention of chemists to some relations subsisting between certain triads—relations, in which the numbers indicative of combining quantities seem to bear a strict proportionality to certain qualities of each member of the triad. The three simple bodies—chlorine, iodine, and bromine—well illustrate the ideas of the celebrated French philosopher. Every chemist is aware of the fact that the three elements above mentioned manifest a certain similarity to each other in many respects, so that in all chemical systems they are described as belonging to one and the same group. Thus, for example, all three are endowed with a pungent odour of the same quality; all three give rise, by combination, to analogous compounds; all three are volatile. Looking at the respective degrees of their cohesive state, we find iodine (a solid) at one end of the series, bromine (a liquid) in the middle, and chlorine (a gas) at the other end; thus presenting a well marked gradation. The same remark holds good, in general, for the degree of energy with which each member of the triad enters into chemical combinations. Several other aspects of viewing the three will occur to chemists; all suggestive of the general idea that chlorine and iodine are respectively the extremes of a triple arrangement, of which bromine is the mean. But the most remarkable coincidence in reference to this subject has been pointed out by M. Dumas, and it is this:—If the equivalent numbers of chlorine and iodine (the extremes) be added together, and their mean proportional obtained by division by 2, the result of this operation is the equivalent number of bromine. Thus,

Atomic, or equivalent weight of chlorine . . .	35
" . of iodine . . .	125
	160

Half that sum $\frac{2)160}{80}$ is the atomic weight of bromine.

"Thus it follows," to use the figurative language of M. Dumas, "if we could by any means cause the union of half an atom of chlorine with half an atom of iodine, we might hope to create an atom of bromine." The language is so far figurative, that to effect the division of an atom, that is to say *an indivisible thing*, is obviously impossible; but it is not irrational to speculate on the divisibility of a force.

Leaving the triad, chlorine, bromine, and iodine, that of sulphur, selenium, and tellurium, may be selected as demonstrative of similarly existing relations. These three bodies are well known by chemists to be isomeric, that is to say, capable of mutually replacing each other in chemical combinations. Of the three, sulphur is the most volatile, selenium the next, tellurium least of all. As to their decomposing power, sulphur replaces selenium, selenium tellurium; in short, the remarks applied to the triad of chlorine, bromine, and iodine, will also apply here. Now the equivalent or combining weight of sulphur is 16, of tellurium 64, and half the sum of these extremes is the number 40—the exact atomic weight of the middle term of the triad—the atomic weight of selenium.

Take again the triad calcium, strontium, and barium. Without stopping to indicate the various analogies of these bodies, it will be sufficient to remark that chemists universally recognise their similarity. In this scale of analogous qualities, calcium and barium are the extremes, strontium is the mean. The atomic or equivalent weights of the three are as follow:—

Calcium	20
Strontium . . .	44
Barium	68 *

And it will be evident at a glance that there exists here a harmony between the chemical qualities and the numeral exponent of their combining proportion as before; for 68 plus 20 divided by 2 is equal to 44, the atomic number of strontium. Then, again, to employ the language of M. Dumas, if we could "by any means effect the union of half an atom of barium with half an atom of calcium, we should have one atom of strontium as the result."

Lithium, sodium, and potassium, constitute another well marked and universally recognised chemical triad. The similarity between these bodies is too evident to need being pointed out. Of the three, lithium is the least individualised alkaline metal; potassium the most individualised; sodium, as every chemist knows, stands intermediately; and here again, referring to the respective equivalent numbers, there is a numeral accordance similar to the one pointed out in the preceding examples.

Such an extraordinary symmetry of chemical qualities with numeral exponents can scarcely be assumed to be a matter of chance; still less can it be averred that the figures on which these deductions are based have been, in any case, much strained to accord with the opinions of M. Dumas, although inorganic chemistry affords the most palpable examples of the correlation between material qualities and numeral exponents; nevertheless, the French philosopher believes this correlation to be far more widely recognisable. Thus many chemists, and M. Dumas amongst the number, have regarded

* It should be remarked that some of the atomic numbers assumed by M. Dumas, and here employed, vary to a slight extent from those generally accepted—not enough, however, to invalidate his doctrine.

certain organic bodies as analogous to the metals. Of this kind are the three organic radicals—

$$C_2 \quad H_2 \quad O$$
$$C_4 \quad H_4 \quad O$$
$$C_6 \quad H_7 \quad O$$

which may be regarded as three several oxides of an isomeric triad, analogous to those already adverted to in the inorganic kingdom. Slight examination will prove the law also holds good in the latter case. Omitting the oxygen in the three preceding substances, half the sums of the extremes will be equal to the mean. Indeed, M. Dumas sees in these manifestations a general law, which may be thus expressed:—When three bodies having qualities precisely similar, though not identical, are arranged in the succession of their chemical powers, there will be also a successive arrangement of their numeral powers, indicated by the respective equivalent numbers of the substances.

This symmetry between chemical and numeral function suggests, as M. Dumas remarks, the possibility of transmutation—yet not transmutation in the old alchemical sense. Chemists see no manifestations of a tendency of being able to convert lead into silver or gold. These metals are not chemically conformable. One cannot take the others place by substitution. They are not isomeric. The probability, M. Dumas imagines, is that our first instances of metallic transmutation will effect the physical state merely without affecting chemical composition, analogous to many known cases amongst non-metallic elements. Thus, carbon as charcoal is widely different in its physical relations from carbon as the diamond. Sulphur and phosphorus respectively assume two forms, as is well known. Why may not a metal be similarly endowed?

Of Elective Affinity.—An important law of affinity, deduced chiefly from the phenomena of chemical decomposition, is, that one body has not the same force of affinity towards a number of others, but attracts them unequally. Thus A will combine with B in preference to C, even when these two bodies are presented to it under equally favourable circumstances. Or when A is united with C, the application of B will detach A from C, and we shall have a new compound, consisting of A and B, C being set at liberty. Such cases are examples of what is termed in chemistry *simple decomposition*, by which it is to be understood that a body acts upon a compound of two ingredients, and unites with one of its constituents, leaving the other at liberty. And as the forces of affinity of one body to a number of others vary, this body has been metaphorically represented as making an election; and the affinity has been called *single elective affinity*. Thus, if to liquid hydrochlorate* of lime, consisting of lime and hydrochloric acid, we add potassa, the lime falls down in the state of a powder, or is *precipitated*. Of facts of this kind a great variety has been comprehended in the form of tables, the first idea of which occurred nearly a century ago to Geoffroy, a French chemist. The substance, whose affinities are to be expressed, is placed at the head of a column, and is separated from the rest by a horizontal line. Beneath this line are arranged the bodies with which it is capable of combining, in the order of their respective forces of affinity; the substance which it attracts most strongly being placed nearest to it, and that for which it has

* What is here called hydrochlorate of lime may really be chloride of calcium; but the latter term would not be expressive in the case under consideration. Under the head of Chlorine and Hydrochloric Acid, the condition of chlorine in aqueous solution will be fully explained.

the least affinity at the bottom of the column. The affinities of hydrochloric acid, for example, are exhibited by the following series:—

HYDROCHLORIC ACID.

Oxide of silver,
Potassa,
Soda,
Baryta,
Strontia,
Magnesia,
Ammonia, &c., &c.

Chemistry, indeed, presents innumerable examples in which this apparent election takes place. A few more leading examples may be noticed. If hydrochloric acid be cautiously added to a mixture of lime and alumina, not a particle of the latter will be attacked until the lime has been quite dissolved; thus creating the impression that the acid and lime were endowed with a sort of reciprocal preference for each other. Nitric acid is capable of acting both upon iron and upon copper, red nitrous acid fumes being in either case evolved; yet if nitric acid be poured upon iron and copper, both in contact, not a particle of copper will be attacked until the iron has been all dissolved. If iodine be brought into contact with hydrosulphuric acid gas, sulphur is expelled, and the iodine and hydrogen unite, forming hydriodic acid gas. If chlorine be mixed with the hydriodic acid gas thus formed, decomposition will again ensue; hydrochloric acid will be formed, and iodine liberated. Nitrate of silver constitutes the starting point of a very interesting series of simple decompositions. If a globule of mercury be thrown into a solution of this salt, the mercury is dissolved, forming nitrate of mercury, and a proportionate amount of silver thrown down. If copper be immersed in nitrate of mercury, mercury is thrown down and copper dissolved, forming nitrate of copper. In like manner, continuing the series, metallic lead will separate copper from nitrate of copper, and metallic zinc will separate lead from nitrate of lead.

It must be here stated, in anticipation of another part of our subject not yet discussed, that the compounds termed in the preceding statement nitrate of copper, of silver, of mercury, &c., are, respectively, nitrates of the oxides of these metals; hence the appellations, nitrate of the *oxide of silver*, &c., would have been more correct: although the expression is usually abbreviated. From this explanation it will appear that the order of separation of the metals, silver, mercury, copper, and lead, is really the order of their separation from oxygen. Consequently, we may now arrange the order of decomposition for the specified substances, as regards oxygen and hydrogen respectively, as follows:—

HYDROGEN.	OXYGEN.
Chlorine	Zinc
Iodine	Lead
Sulphur	Copper
	Mercury
	Silver

If the order of decomposition for any given series were invariable, then it would be

easy by means of tables, such as those drawn up by Geoffroy, to specify the relative strength of affinity subsisting between any number of bodies which might have once been submitted to investigation. But various circumstances demonstrate that such tables merely indicate the order of decomposition under one particular set of conditions, and are by no means to be accepted as a true measure of affinity. The force of the objection just offered will be rendered apparent by reflecting on the following circumstances.

If aqueous vapour be passed over red-hot iron, oxide of iron is formed and hydrogen liberated, thus giving rise to an impression, if the theory of Geoffroy be adopted, that oxygen possesses a greater affinity for iron than it has for hydrogen; yet, by varying the conditions, it is possible to obtain a testimony directly opposed to the former. If oxide of iron be submitted to the action of hydrogen gas, at an elevated temperature, the oxide is decomposed, and water and metallic iron result. Judging from the testimony of this experiment, it would appear that oxygen has a greater affinity for hydrogen than for iron.

If potassium be thrown into water, so violent is the tendency which the alkaline metal manifests for oxygen that water is decomposed, and combustion ensues. If metallic iron be thrown into water, only a very slow oxidation of the iron, after the lapse of a considerable time, takes place. Hence, were there no opposing testimony, it would seem clearly deducible from the result of these experiments that potassium has greater affinity than iron for oxygen. Yet the actual method of obtaining the metal potassium consists in exposing its oxide (potash), at a white heat, to the decomposing agency of metallic iron. If sulphuric acid be poured into a solution of borax (borate of soda), decomposition ensues, sulphate of soda being formed, and boracic acid deposited. Yet, if boracic acid be heated with sulphate of soda, both dry; then borax results, and sulphuric acid is expelled.

By thus varying the treatment, results the most opposite to those which might have been anticipated are obtained. A very remarkable example is furnished by the action of silicic acid on common salt, at a high temperature. In all ordinary moist operations silicic acid, or silica, is endowed with such weak acid powers that they can scarcely be recognised; yet, under conditions of high temperature, these powers are greatly elevated. The most common plan of glazing porcelain depends upon this fact: whilst the unglazed, or biscuit ware, is still glowing, a handful of common salt being thrown upon it, decomposition ensues—silicate of soda is formed, and chlorine is expelled.

Again, if hydrochlorate of lime be mixed with an aqueous solution of carbonate of ammonia, carbonate of lime is thrown down and hydrochlorate of ammonia results; yet, if the two be heated together, without water, no decomposition ensues—carbonate of ammonia is evolved and hydrochlorate of lime remains.

All these instances—and many others might be cited—prove indubitably that the force of affinity is subjected to modifications by so great a number of causes, that the tables of decomposition drawn up by Geoffroy can by no means be considered indicative of the relative forces of affinity between the different substances specified in the table.

The inconclusiveness of the so-called tables of affinity of Geoffroy was first pointed out by the celebrated Berthollet. When he propounded his objections, the laws of definite proportionalism were not established; and, pushing his objections to an extreme, he denied the existence of attraction as a separate force. He maintained that the formation of any binary compound—and none other than binary compounds were known in his time—was not due to the operation of any distinctive force, but

to the fact that the elements forming such a body happened to generate in certain proportions, a result of maximum cohesion. Thus, we know that 40 parts of sulphuric acid and 76 parts of baryta constitute the insoluble sulphate of baryta; and we believe the determinate ratio of this combination to be explicable on the assumption of the definite proportionalism of chemical compounds. Berthollet, however, assumed that the combination of sulphuric acid with baryta, in these proportions, depended on the fact that no other combination of the two yielded a result of equal insolubility.

The deposition of sulphate of baryta, when sulphuric acid is mixed with a barytic salt, furnished one of the instances cited by Berthollet of the modification of affinity by *cohesion of the resultant.* In cases where the result of combination does not form any compound of great cohesion—or, in other words, of great insolubility—then, according to Berthollet, the ingredients might combine together in all possible proportions; and the final result, obtained by evaporation, or otherwise, would be determined by the cohesive force then brought into play.

If we discard the fundamental error of ignoring such a force as chemical attraction; if we admit it to exist, but assume that its normal action is modified by collateral circumstances—then the remarks of Berthollet will generally hold good. This philosopher has the merit of awakening attention to a very large series of facts, and has corrected a dogma altogether incompatible with the testimony of experiment. There can be no doubt that, in many cases of solution, the distribution of two acids between one base does actually occur, as indicated by Berthollet. Thus, sulphate of copper is blue, hydrochlorate of copper green; and if hydrochloric acid be added to a solution of sulphate of copper, a green colour results; yet, on evaporation, hydrochloric acid passes away, and sulphate of copper reappears. In this instance it is scarcely possible to resist the testimony that in the solution chloride of copper existed. This result, however, is by no means invariable, as will appear from a consideration of the following experiment. Sulphuric acid, and boracic acid, both redden litmus paper; but the tint of redness is so different that it may easily be recognized. Now, if a solution of borax be decomposed by the addition of sulphuric acid, and the solution frequently tested during the operation, by means of litmus paper, it will be found that not the slightest indication of sulphuric acid is recognizable until every particle of the borax has been decomposed. This evidence seems to demonstrate the existence of chemical attraction or affinity as a self-existing specific force; otherwise, there appears no reason wherefore the soda of the borax should not be divided between the two acids. That a base is thus divided in some cases—in the instance, for example, just cited—where hydrochloric acid was supposed to be added to a solution of sulphate of copper, is easily explicable on the supposition that the affinities of the two acids, under the conditions of the experiment, were equally balanced.

The doctrine of Berthollet, maintained with all the powerful argumentation of that highly-gifted philosopher, would, if established, have shattered the structure of Chemistry to its base. The progress of investigation has satisfied chemists that a specific force of attraction of affinity does exist; and to this extent the theory of Berthollet is incorrect. It has also satisfied them that so many extraneous causes are in operation to modify the order of decomposition, that no certain knowledge of the power of affinity existing between bodies can be deduced from any one order of decomposition. The causes which modify the action of affinity will be discussed in the following section.

Simple decompositions may be expressed also by another form, contrived by

Bergman. Thus the following scheme illustrates the decomposition of hydrochlorate of magnesia by potassa:—

Hydrochlorate of Potassa.

Hydrochlorate of Magnesia. { Hydrochloric acid. Potassa. Water at 60°. Magnesia. }

Magnesia.

The original compound (hydrochlorate of magnesia) is placed on the outside and to the left of the vertical bracket. The included space contains the original principles of the compound, and also the body which is added to produce decomposition. Above and below the horizontal lines are placed the new results of their action. The point of the lower horizontal line being turned downwards, denotes that the magnesia falls down, or is precipitated; and the upper line, being perfectly straight, shows that the hydrochlorate of potassa remains in solution. If both the bodies had remained in solution, they would both have been placed above the upper line; or, if both had been precipitated, beneath the lower one. If either one or both had escaped in a volatile form, this would have been expressed by placing the volatilized substance above the diagram, and turning upwards the middle of the upper horizontal line. And since decompositions vary under different circumstances, it is necessary to denote, by the proper addition to the scheme, that the bodies are dissolved in water of the temperature of 60°.

The decomposition may be still more effectually represented by the following arrangement of diagram, which is that now most usually adopted:—

Potassa ——————————— Hydrochlorate of potassa.

Hydrochlorate of Magnesia { Hydrochloric acid / Magnesia ▽

No chemical facts can appear, on first view, more simple or intelligible than those which are explained by the operation of single elective affinity. It will be found, however, on a more minute examination, that this force, abstractedly considered, is only one of several causes which are concerned in chemical decompositions, and that its action is modified, and sometimes even subverted, by counteracting forces.

OF THE CAUSES WHICH MODIFY THE ACTION OF CHEMICAL AFFINITY.

The order of decomposition is not, as might be inferred from the law of elective affinity, invariable; but, in certain cases, may even be reversed. Thus, though A may attract B more strongly than either A or B is attracted by C, yet, under some circumstances, C may be employed to decompose partially the compound A B. Again, if we mix together A, B, and C, using the two first in the proportions required to neutralize each other, it will be found in some cases that A and B have not combined to the exclusion of C, but that we have a compound of B with A, and another of B with C, in proportions regulated by the quantities of A and C which have been employed. Facts

of this kind have been long known to chemists. It had been ascertained, for example, before the time of Bergman, that sulphate of potassa, a salt composed of sulphuric acid and potassa, is partly decomposed by nitric acid, although the nitric has a weaker affinity than the sulphuric acid for that alkali. Examples of the same kind have since been multiplied by Berthollet, who asserts that in the following, as well as in other cases, the body first mentioned, in each line, decomposes a compound of the second and third, although its attraction for the second is inferior to that of the third for the second.

1. Potassa separates sulphuric acid from baryta.
2. Lime separates sulphuric acid from potassa.
3. Potassa separates oxalic acid from lime.
4. Nitric acid separates lime from oxalic acid.
5. Potassa separates phosphoric acid from lime.
6. Potassa separates carbonic acid from lime.
7. Soda separates sulphuric acid from potassa.

These instances of *reciprocal decomposition*, and a variety of similar ones, are explained, according to the views of Berthollet, on the following principles:—

Antagonistic Forces.—When two substances are opposed to each other with respect to a third, as in the foregoing examples, they may be considered as antagonist forces; and they share the third body between them in proportion to the intensity of their action. But this intensity, according to Berthollet, depends not only on the *energy of the affinities*, but on the *quantities* of the two bodies opposed to each other. Hence a larger quantity of one of the substances may compensate a weaker affinity, and the reverse. To the absolute weight of a body, multiplied by the degree of its affinity, he has given the name of *mass*, a term in some degree objectionable from the different meaning which is affixed to it in mechanical philosophy. As an illustration, let us suppose (what is not accurate in point of fact) that the affinity of baryta for hydrochloric acid is twice as strong as that of potassa, or that these affinities are respectively denoted by the numbers 4 and 2. In this case the same *mass* will result from 4 parts of baryta as from 8 of potassa: because the same product (16) is obtained in each instance, by multiplying the number indicating the affinity into that denoting the quantity; for 4 (the affinity of baryta) multiplied by 4 (the quantity assumed in this example) is equal to 16; and 2 (the affinity of potassa) multiplied by 8 (its quantity) is also equal to 16. In this case, therefore, to divide equally a portion of hydrochloric acid between baryta and potassa, these bodies should be employed in the proportion of 2 of the former to 4 of the latter.

The influence of quantity explains also the difficulty which, in many instances, is observed in effecting the total decomposition of a compound of two principles by means of a third. The immediate effect of a third body C, when added to a compound A B, is to abstract from B a portion of the substance A; and, consequently, a portion of B is set at liberty, the attraction of which for A is opposed to that of the uncombined part of C. The farther this decomposition is carried, the greater will be the proportion of B, which is brought into an uncombined state; and the more powerfully will B oppose any farther tendency of C to detach the substance A. At a certain point, the affinities of B and C for A will be exactly balanced, and the decomposition will proceed no farther. In several cases, it is acknowledged by Berthollet, a third body separates the whole of one of the principles of a compound; but this he supposes to happen in con-

sequence of the agency of other extraneous forces, the nature of which remains to be pointed out.

Cohesion is a force, the influence of which over the chemical union of bodies has already been explained in a former section; and other illustrations of its interference will be given, when we consider the subject of the limitations to chemical combination.

Insolubility is another force, which essentially modifies the exertion of affinity. It is to be considered, indeed, merely as the result of cohesion, with respect to the liquid in which the effect takes place.

When a soluble substance and an insoluble one are presented, at the same time, to a third, for which they have nearly an equal affinity, the soluble body is brought into the sphere of action with great advantages over its antagonist. Its cohesion at the outset is but little, and by solution is reduced almost to nothing; while that of the insoluble body remains undiminished. The whole of the soluble substance also exerts its affinity at once; while a part only of the insoluble one can oppose its force. Hence the soluble substance may prevail, and may attach to itself the greatest proportion of the third body, even though it has a weaker affinity than the insoluble one to the subject of combination.

Insolubility, however, under certain circumstances, is a force which turns the balance in favour of the affinity of one body when opposed to the affinity of another. For example, if to the soluble compound, sulphate of soda, we add baryta, the new compound, sulphate of baryta, is precipitated the instant it is formed; and, being removed from the sphere of action, the soda can exert no effect upon it by its greater quantity or mass. For the same reason, when soda is added to sulphate of baryta, the sulphate is protected from decomposition both by its insolubility and by its cohesion.

These facts convinced Berthollet that the order of precipitation, which was formerly assumed as the basis of tables of affinity, can no longer be considered as an accurate measure of that force; and that the body which is precipitated may, in some cases, be superior in affinity to the one which has caused precipitation. In these cases, a trifling superiority in affinity may be more than counterbalanced by the cohesive force, which causes insolubility.

Great Specific Gravity is a force which must concur with insolubility or cohesion in originally impeding combination; and, when chemical union has taken place, it must come in aid of affinity, by removing the new compound from the sphere of action. It is scarcely necessary to enlarge upon the operation of a force, the nature of which must be so obvious.

Elasticity.—Cohesion, it has already been stated, may prove an impediment to combination; and, on the other hand, it is possible that the particles of bodies may be separated so widely, as to be removed out of the sphere of their mutual attraction. Such appears to be the fact with regard to a class of bodies called airs or gases. The bases of several of these have powerful attractions for the bases of others, and for various liquids, and yet they do not combine on simple admixture, but strong mechanical pressure brings their particles sufficiently near to be within the influence of their mutual attraction, and combination then ensues.

Again, if two bodies, one of which has an elastic and the other a liquid form, be presented at the same time to a solid, for which they have both an affinity, the solid will unite with the liquid in preference to the gas. Or, if we add to the compound of an elastic substance with an inelastic one, a third body also inelastic, the two which are inelastic combine, to the exclusion of the elastic body. For example, if to the com-

pound of potassa and carbonic acid we add sulphuric acid, the latter acid, acting both by its affinity and its quantity, disengages a portion of carbonic acid. This, by its elasticity, is removed from the sphere of action, and presents no obstacle to the farther operation of the sulphuric acid. Hence elastic bodies act only by their affinity; whereas liquids act both by their affinity and quantity conjoined. And though the affinity of the liquid, abstractedly considered, may be inferior to the affinity of the elastic body, yet, aided by quantity, it prevails. In the above instances, the whole of the elastic acid may be expelled by the fixed acid; whereas, as it has already been observed, decomposition is frequently incomplete, if the substance which is liberated remain within the sphere of action.

The influence exercised by elasticity in modifying the play of affinity, may be illustrated by restraining the elastic substance and not permitting its escape. Thus, if carbonate of lime be exposed to red heat, carbonic acid escapes and lime remains; but if the heating be conducted in a close vessel under great pressure, then carbonate of lime may be fused unchanged. In this way, the greater part, if not all the marble existing in Nature has been evidently formed.

Efflorescence is a circumstance which occasionally influences the exertion of affinity; but this is only of very rare occurrence. The simplest example of it is that of lime, and hydrochlorate of soda. When a paste composed of these two substances, with a great excess of lime, is exposed to the air in a moist state, the lime, acting by its quantity, disengages soda from the common salt, which appears in a dry form, on the outer surface of the paste, united with carbonic acid absorbed from the atmosphere. In this case the soda, which is separated, being removed from contiguity with the interior part of the mass, presents no obstacle to the farther action of the lime, and the decomposition is carried farther than it would have been, had no such removal happened.

Temperature.—The influence of *temperature* over chemical affinity is extremely important; but, at present, a very general statement only of its effect is required. In some cases an increased temperature acts in promoting, and at others in impeding, chemical combination; it materially affects also the order of decompositions.

An increased temperature promotes chemical union by diminishing or overcoming cohesion. Thus metals unite by fusion, and several salts are more soluble in hot than in cold water. Whenever heat is an obstacle to combination, it produces its effect by increasing elasticity. Hence water absorbs a less proportion of ammonia at a high than at a low temperature. A reduction of the temperature of elastic bodies, by lessening their elasticity, facilitates their union with other substances. In certain cases, an increased temperature has the effect both of diminishing cohesion and increasing elasticity. When sulphur is exposed to oxygen gas, no combination ensues until the sulphur is heated; and, though the elasticity of the gas is thus increased, the diminution of cohesion of the solid is more than proportionate, and chemical union ensues between the two bodies.

Electrical state of bodies has a most important influence over their chemical union. This, however, is a subject which will be treated at length in a subsequent chapter on *Electro-chemistry*.

Mechanical pressure is another force which has considerable influence over chemical affinity. With respect to solid bodies, its agency is not frequent; but we have unequivocal examples of its operation in cases were detonation is produced by concussion. The effects of pressure are chiefly manifested in producing the combination of

aeriform bodies either with solids, with liquids, or with each other; and in preserving combinations, which have been already formed, under circumstances tending to disunite them. Chalk, for example, is a compound of lime and carbonic acid; and these bodies, by the simple application of an intense heat, are separable from each other; but, under strong pressure, a heat may be applied sufficient to melt the chalk, without expelling the carbonic acid.

Such are the most important circumstances that modify the exertion of chemical affinity. Of their influence, sufficient illustrations have been given to prove, that in no case of combination and decomposition are we to consider the force of affinity abstractedly, but are to take into account the agency of other powers, as cohesion, quantity, insolubility, elasticity, efflorescence, and temperature. But we cannot concede to Berthollet that these accessary forces are, of themselves, sufficient to explain all the phenomena to which he has applied them; for no one can doubt that chemical decompositions and combinations are, in a great majority of cases, produced independently of those accessary forces, and are due to the different degrees of affinity inherent in the heterogeneous particles of bodies. Still less can the principles of Berthollet be admitted, to account for the uniformity of proportions in which bodies combine; for besides that the cause assigned is inadequate to the effect, we find in the atomic theory a far more satisfactory explanation of the union of bodies in definite and in multiple proportions. That the theory of Berthollet is of much more limited application than he supposed, will appear also from the following considerations.

1. It has been shown by Professor Pfaff, of Kiell (77 Ann. de Chim. p. 259), that, in various cases, where two acids are brought into contact with one base, the base unites with one acid, to the complete exclusion of the other. When, for example, to a given weight of lime, quantities of sulphuric and tartaric acids are added, either of which would exactly neutralize the lime, the sulphuric acid unites with the lime to the entire exclusion of the tartaric. Similar evidence of a superior affinity of the sulphuric acid, over that of the oxalic, is obtained by placing these acids in contact with as much oxide as had it would exactly saturate either of them. Now, in these instances, and in a [illegible] others of the same kind, we cannot explain the effect by the extraneous [illegible] of cohesion, which, judging from the degree of insolubility, is greater in the [illegible] in the new compound, and [illegible] have had no share in the pro- [illegible]

2. [illegible] Berthollet, to show [illegible] most probably [illegible] concerned: [illegible] into action. [illegible] displaced [illegible] from [illegible]

[illegible] and B. for [illegible] of A and [illegible] brought [illegible] affinity [illegible] when [illegible] and the [illegible] of

potassa, composes a new salt, consisting of sulphate of potassa with an additional proportion of sulphuric acid.

4. It is a strong objection to the theory of Berthollet that, in some cases, decompositions happen, which, according to his views, ought not to take place; and that in others decompositions do not ensue, which the theory would have led us to have anticipated.

5. The theory is objectionable, inasmuch as, in several instances, forces are supposed to operate, before the bodies exist to which those forces are attributed. It is inconceivable, for instance, that the cohesion, or insolubility, of sulphate of baryta, can have any share in producing the decomposition of sulphate of potassa by that earth; for the insolubility of sulphate of baryta can have no agency till that compound is formed, which is the very effect to be explained.

Notwithstanding these objections to the theory of Berthollet, when carried so far as has been done by its author, in the explanation of chemical phenomena, it must still be admitted that the extraneous forces, pointed out by that acute philosopher, have some influence in modifying the effects of chemical affinity. But these forces are entitled only to be considered as secondary causes, and not as determining combinations or decompositions, nor as regulating the proportions in which bodies unite, independently of the superior force of chemical affinity.

Forces of Affinity.—The affinities of one body for a number of others are not all of the same degree of force. This is all that the present state of our knowledge authorises us to affirm; for we are ignorant *how much* the affinity of one body for another is superior to that of a third. The determination of the precise forces of affinity would be an important step in chemical philosophy: for its phenomena might then be reduced to calculation; and we should be enabled to anticipate the results of experiment. That the force of chemical affinity must be prodigiously great, is evident from its effect in preserving the combination of water with some bodies (the alkalies for instance) when exposed to a violent heat, notwithstanding its great expansive force, and though water is not essential to the constitution of those bodies.

The observed order of decomposition, it has already been stated, does not enable us to assign the order of the forces of affinity; because, in many decompositions, extraneous forces are concerned. Other methods of determining the problem have therefore been attempted.

When the surface of one body is brought into contact with another surface of the same kind, as when the smooth surfaces of a divided leaden bullet are pressed together, they adhere by the force of cohesion, their particles being all of the same kind. But when the surfaces of different bodies are thus brought into apparent contact, it seemed to Guyton reasonable to suppose that their adhesion arose from chemical affinity, because their particles were of different kinds. He proposed, therefore, the comparative force, with which different surfaces adhere, as a measure of chemical affinity. His experiments were made on plates of different metals, of precisely the same size and form, suspended by their centres from the arm of a sensible balance. The lower surfaces of these plates were successively brought into contact with mercury, which was changed for each experiment, and the weight was observed, which it was necessary to add to the opposite scale, in order to detach the several metals. Those which required the largest weight were inferred to have the greatest affinity; and it is remarkable that the order of affinities, as determined in this

way, correspond with the affinities as ascertained by other methods. The following were the results:—

Gold adhered to mercury with a force of	446 grains.	Zinc	204 grains.
Silver	429	Copper	142
Tin	418	Antimony	126
Lead	397	Iron	115
Bismuth	372	Cobalt	8

This method, it must be obvious, is of too limited application to be of much utility; for few bodies have the mechanical conditions which enable us to subject them to such a test. How, for example, could the affinities of acids for alkalies be examined on this principle? It may be doubted also, whether, in the cases to which it may be applied, it does not measure facility of combination rather than the actual strength of affinity.

To determine accurately the relative forces of affinity which a body (A) of one class exerts towards a number of others (X Y Z) of a different class, and to express them by numbers, Mr. Kirwan proposed the quantities of the latter which are required to produce neutralization. With this view, he made numerous experiments; but as their results have been shown to be inaccurate, I shall employ, in explaining the principle of his method, the more correct numbers which have been since ascertained by other chemists.

40 Parts of Sulphuric Acid require for Neutralization	48 Parts of Potassa require
76 parts of baryta.	54 parts of nitric acid.
52 " of strontia.	44 " of carbonic acid.
48 " of potassa.	40 " of sulphuric acid.
32 " of soda.	36 " of hydrochloric acid.
28 " of lime.	
20 " of magnesia.	
17 " of ammonia.	

In judging of the affinities of the same acid for different bases, Mr. Kirwan assumed that they are represented by the numbers indicating the quantities of each base required for neutralization. Thus, because 40 parts of sulphuric acid neutralize 76 of baryta and 48 of potassa, he concluded the affinity of the former to that of the latter to be in the proportion of 76 to 48. So far the inference corresponds with the order of decomposition; baryta, for example, takes sulphuric acid from potassa. But even in this case, we are not entitled to conclude that these numbers express accurately the relative affinities of different bases for the same acid. And if we apply the rule to the numbers in the second column, we shall find it to fail entirely; for both nitric and carbonic acids are separated from potassa by sulphuric acid, although the capacity of saturation in the latter is expressed by the lowest number. Mr. Kirwan was, therefore, driven to the necessity of establishing a precisely opposite rule in determining the affinities of different acids for the same base, and of assuming that they are *inversely* proportionate to the quantities of the saturating acid. Thus the affinity of nitric acid for potassa would be represented by 40, and that of sulphuric acid by 54. This, however, involves a contradiction; since it is implied that in one set of cases a greater quantity of the

saturating principle indicates a stronger affinity, and that in the other a less quantity implies a stronger affinity.

Since neutralization is an effect of chemical affinity, which must in all cases bear a proportion to its cause, it was argued by Berthollet that the substance which, in the *smallest quantity*, neutralizes another, is the one possessing the greatest affinity. Thus, because 17 parts of ammonia go as far in neutralizing a given weight of any acid as 78 of baryta, he concluded that the relative affinities of ammonia and baryta for acids are inversely as those numbers. That ammonia is expelled from all acids by baryta, he explains by the action of an extraneous force (elasticity) which exists in ammonia, and turns the balance in favour of the fixed bases. But this explanation is liable to an obvious objection; for, as the elasticity of ammonia is suppressed by combination with sulphuric acid, what (it may be asked) but a stronger affinity for that acid, existing in all the substances standing above ammonia in the Table, can determine the first commencement of decomposition?

It is sufficient to have given this brief view of the methods employed to express numerically the forces of affinities, to show that the problem has not yet been solved; that they cannot be appreciated by the adhesion of surfaces; and that they are not denoted by those equivalent numbers, or atomic weights, that have been deduced from the proportions in which bodies combine.

Of Complex Affinity.—Under the more general name of *complex affinity*, Berthollet includes all those cases of decomposition which have hitherto been considered as produced by the action of four affinities, commonly denominated *double elective affinity*. It frequently happens that the compound of two bodies cannot be destroyed either by a third or a fourth separately applied; but if the third and fourth be combined, and placed in contact with the former compound, a decomposition or exchange of principles will ensue. Thus, when lime water is added to a solution of the sulphate of soda, no decomposition happens, because the sulphuric acid attracts soda more strongly than it attracts lime. If nitric acid be applied to the same compound, its principles remain undisturbed, because the sulphuric acid attracts soda more strongly than the nitric. But if the lime and nitric acid, previously combined, be mixed with the sulphate of soda, a double decomposition is effected. The lime, quitting the nitric acid, unites with the sulphuric; and the soda, being separated from the sulphuric acid, combines with the nitric. These decompositions are rendered more intelligible by the following kind of diagram, suggested by Bergman, the form of which may be readily modified, so as to adapt it to more complicated cases. A more convenient method, however, of indicating chemical decompositions is the one given at page 30.

Nitrate of Soda 86

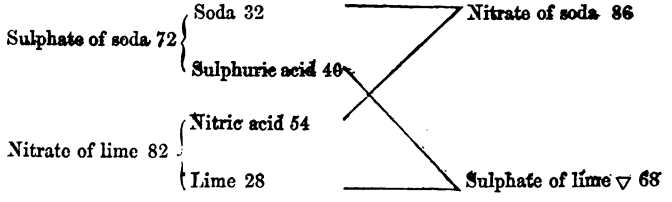
Sulphate of Soda 72	Sulphuric acid 40	Nitric acid 54	Nitrate of Lime 82
	Soda 32	Lime 28	

Sulphate of Lime 68

On the outside of the vertical brackets are placed the original compounds; and above and below the diagram, the new compounds. The upper line, being straight,

indicates that the nitrate of soda remains in solution; and the middle of the lower line, being directed downwards, that the sulphate of lime is precipitated.

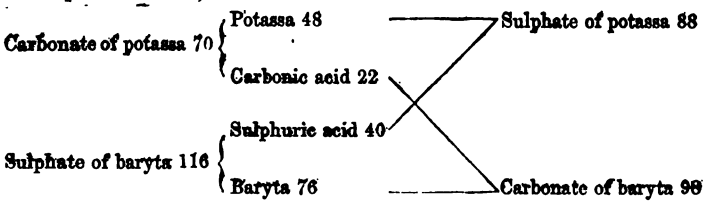
The figures, which form part of the diagram, are the equivalent numbers of the original and newly-formed compounds, as well as of their proximate elements. Thus, by mingling 72 parts of sulphate of soda, consisting of 32 soda and 40 sulphuric acid, with 82 of nitrate of lime, = 54 nitric acid and 28 lime, the products are 68 of sulphate of lime (28 base + 40 acid), and 86 nitrate of soda (32 base + 54 acid). When the original compounds are, as in this instance, perfectly neutral, the new products will be found equally so. This general fact, first noticed by Wenzel, is a consequence of the law of combination in definite proportions; for, under all circumstances, equivalent quantities of acids and bases, whether directly united or mutually transferred, as in the above instance, must exactly neutralize each other.



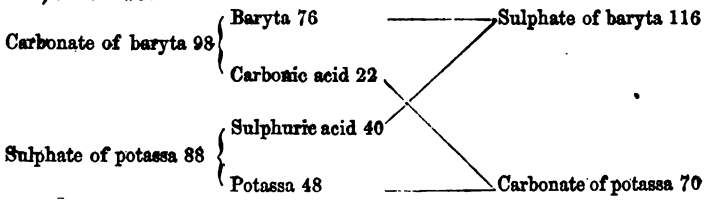
To the affinities tending to produce decomposition Mr. Kirwan gave the name of *divellent affinities*, and to those preserving the original compounds that of *quiescent* affinities. These he attempted to express by numbers, so chosen as to enable him to anticipate the results of experiment. It is sufficient to observe, that, for reasons which I have already stated, this attempt entirely failed. We may still, however, retain the expressions *divellent* and *quiescent*, as a convenient mode of speaking of a certain class of chemical decompositions. Over these phenomena, the extraneous causes, pointed out by Berthollet, appear also to have considerable influence. That of *quantity* is shown by the fact, that if two salts be mixed together in certain proportions, decomposition will ensue; but not if mixed in other proportions. Thus, from the mingled solutions of two parts of hydrochlorate of lime and one of nitrate of potassa, we obtain hydrochlorate of potassa; but not from equal weights of the two salts. Insolubility, or precipitation, has also a considerable influence on the result. When this occurs, the influence of quantity is destroyed, as in the case of sulphate of potassa and hydrochlorate of baryta. Elasticity, and an increased temperature (which operates by increasing elasticity), and the reverse of this, or a greatly *diminished* temperature, have also a powerful influence in promoting the action of complex affinities. Thus of four principles, two of which are volatile and two fixed, the two which are volatile will be most disposed to unite together at a high temperature, even though, under other circumstances, they may take a different order of arrangement. Thus, at common temperatures, carbonate of ammonia decomposes sulphate of lime; but if a mixture of sulphate of ammonia and carbonate of lime be heated, we obtain carbonate of ammonia and sulphate of lime. The nature of the fluid, in which salts are dissolved, has also an important influence on their tendency to mutual decomposition (Ann. de Chim. et de Phys. iv. 366).

Other exceptions to the laws of affinity, affecting double as well as single decompositions, have been classed together under the name of *reciprocal affinity*. They occur

ly in the mutual action of soluble carbonates and insoluble salts on each other, and mited to those cases in which an insoluble compound is one of the products. For ple, carbonate of potassa and sulphate of baryta, in quantities denoted by their ic numbers, when long boiled together with water, form carbonate of baryta and ate of potassa. Thus,



ut if we reverse the experiment, and digest together equivalent quantities of ate of potassa and carbonate of baryta, we have still a mutual exchange of acids ases, as follows :—



ow, the results of the latter experiment would appear, on first view, quite incon- it with the order of affinities established by the former. But when the facts are ly examined, it will be found that in neither case is the exchange of principles lete; for in both the decomposition ceases as soon as the newly-formed compounds acquired a certain proportion to the original ones and to each other. In the case ited by the first diagram, the alkaline energy of the soluble carbonate gradually nes less as its quantity diminishes, and as the solution approaches nearer and r to neutralization. In the second case, the decomposition cannot be carried d that point at which the carbonate of baryta and sulphate of potassa, remaining composed, are in certain proportions to each other. These facts have been care- investigated and ingeniously explained by Dulong, at greater length than would nsistent with the objects of this work. I refer, therefore, to his Memoir in the vol. of the Annales de Chimie, which has been translated into the 35th and 36th of Nicholson's 8vo Journal, and published in an abridged form in the 41st vol. of Philosophical Magazine.

Experimental Illustrations.—For these experiments, a few wine-glasses, or, eference, deep ale-glasses, will be required; and a Florence flask for performing olutions.

. *Some bodies appear to have no affinity for each other.*—Oil and water, mercury and r, or powdered chalk and water, when shaken together in a vial, do not combine, il or water always rising to the surface, and the mercury or chalk sinking to the om.

I. *Examples of chemical affinity, and its most simple effect, viz., solution.*—Sugar or

common salt disappears or dissolves in water; chalk in dilute hydrochloric acid. Sugar and salt are therefore said to be *soluble* in water, and chalk in hydrochloric acid. The liquid, in which the solid disappears, is termed a *solvent* or *menstruum*. Chalk or sand, on the contrary, when mixed with water by agitation, always subsides again. Hence they are said to be *insoluble*.

III. *Influence of mechanical division in promoting the action of chemical affinity, or in favouring solution.*—Lumps of chalk or marble dissolve much more slowly in dilute hydrochloric acid than equal weights of the same bodies in powder. Hydrochlorate of lime, or nitrate of ammonia, cast, after liquefaction by heat, into the shape of a solid sphere, is very slowly dissolved; but with great rapidity when in the state of a powder or of crystals. When a lump of the Derbyshire spar (fluoride of calcium) is immersed in concentrated sulphuric acid, scarcely any action of the two substances on each other takes place; but if the stone be finely pulverized, and then mingled with the acid, a violent action is manifested, by the copious escape of vapours of hydrofluoric acid. In the common arts of life, the rasping and grinding of wood and other substances are familiar examples.

IV. *Hot liquids, generally speaking, are more powerful solvents than cold ones.*—To four ounce-measures of water, at the temperature of the atmosphere, add three ounces of sulphate of soda in powder. Only part of the salt will be dissolved, even after being agitated some time. Apply heat, and the whole of the salt will disappear. When the liquor cools, a portion of salt will separate again in a regular form, or in *crystals*. This last appearance affords an instance of *crystallization*.

To this law, however, there are several exceptions; for many salts, among which is chloride of sodium, or common salt, are equally, or almost equally, soluble in cold as in hot water. Hence, a hot and saturated solution of chloride of sodium does not, like the sulphate, deposit crystals on cooling. To obtain crystals of the chloride, and of other salts which observe a similar law as to solubility, it is necessary to evaporate a portion of the water; and the salt will then be deposited, even while the liquor remains hot. In general, the more slow the cooling, or evaporation, of saline solutions, the larger and more regular are the crystals.

V. *A very minute division of bodies is effected by solution.*—Dissolve two grains of sulphate of iron in a quart of water, and add a few drops of this solution to a wine-glassful of water, into which a few drops of tincture of galls have been stirred. The dilute infusion of galls will speedily assume a purplish hue. This shows that every drop of the quart of water, in which the sulphate of iron was dissolved, contains a notable portion of the salt.

VI. *Some bodies dissolve much more readily and copiously than others.*—Thus, an ounce-measure of distilled water will dissolve half its weight of sulphate of ammonia, one-third its weight of sulphate of soda, one-sixteenth of sulphate of potassa, and only one five-hundredth its weight of sulphate of lime.

VII. *Mechanical agitation facilitates solution.*—Into a wine-glassful of water, tinged blue, with the infusion of litmus, let fall a small lump of solid tartaric acid. The acid, if left at rest, even during some hours, will only change to red that portion of the infusion which is in immediate contact with it. Stir the liquor, and the whole will immediately become red.

VIII. *Bodies do not act on each other, unless either one or both be in a state of solution, or at least contain water.*—1. Mix some dry tartaric acid with dry bi-carbonate of soda, and grind them together in a mortar. No combination will ensue till water is added; which, acting the part of a solvent, promotes the union of the acid and alkali, as

appears from a violent effervescence. It has been shown by Link, that the water of crystallization, existing in certain salts, acts as free water in occasioning chemical action. For example, acetate of lead and sulphate of copper, both in crystals, become green when triturated together, a proof of the mutual decomposition of those two salts.

2. Spread thinly, on a piece of tinfoil, three or four inches square, some dry nitrate of copper,* and wrap it up. No effect will follow. Unfold the tinfoil, and, having sprinkled the nitrate of copper with the smallest possible quantity of water, wrap the tinfoil up again as quickly as possible, pressing down the edges closely. Considerable heat, attended with fumes, will now be excited; and, if the experiment has been dexterously managed, even light will be evolved. This shows that nitrate of copper has no action on tin, unless in a state of solution.

IX. *Bodies, even when in a state of solution, do not act on each other at perceptible distances;* in other words, contiguity is essential to the action of chemical affinity.—Thus, when two fluids of different specific gravities, and which have a strong affinity for each other, are separated by a thin stratum of a third, which exerts no remarkable action on either, no combination ensues between the uppermost and lowest stratum. Into a glass jar, or deep ale-glass, pour two ounce-measures of a solution of subcarbonate of potassa, containing, in that quantity, two drachms of common salt of tartar. Under this introduce, very carefully, half an ounce-measure of water, holding in solution a drachm of common salt; and again, under both these, two ounce-measures of sulphuric acid, which has been diluted with an equal weight of water, and allowed to become cool. The introduction of a second and third liquid, beneath the first, is best effected by filling, with the liquid to be introduced, the dropping tube, which may be done by the action of the mouth. The finger is then pressed on the upper orifice of the tube; and the lower orifice being brought to the bottom of the vessel containing the liquid, the finger is withdrawn, and the liquid descends from the tube, without mingling with the upper stratum. When a solution of carbonate of potassa is thus separated from diluted sulphuric acid, for which it has a powerful affinity, by the intervention of a thin stratum of brine, the two fluids will remain distinct and inefficient on each other; but, on stirring the mixture, a violent effervescence ensues, in consequence of the action of the sulphuric acid on the potassa.

X. *Two bodies, having no affinity for each other, unite by the intervention of a third.*—Thus, the oil and water which, in Experiment I., could not, by agitation, be brought into union, unite immediately on adding a solution of caustic potassa. The alkali, in this case, acts as an intermedium. The fact, however, admits of being explained by the supposition, that the oil and alkali form, in the first instance, a compound which is soluble in water.

XI. *Saturation and neutralization illustrated.*—Water, after having taken up as much common salt as it can dissolve, is said to be *saturated* with salt. Hydrochloric acid, when it has ceased to act any longer on lime, is said to be *neutralized*, as is also the lime.

XII. *The properties characterizing bodies, when separate, are destroyed by chemical combination, and new properties appear in the compound.*—Thus hydrochloric acid and lime, which in a separate state have each a most corrosive taste, lose this entirely when

* To prepare nitrate of copper, dissolve the filings or turnings of that metal in a mixture of one part nitric acid and three parts water; decant the liquor when it has ceased to emit fumes; and evaporate it to dryness, in a copper or earthen dish. The dry mass must be kept in a bottle.

mutually saturated; the compound is extremely soluble, though lime itself is very difficult of solution; the acid no longer reddens syrup of violets, nor does the lime change it, as before, to green. The resulting compound, also, hydrochlorate of lime, exhibits new properties. It has an intensely bitter taste; is susceptible of a crystallized form; and the crystals, when mixed with snow or ice, generate a degree of cold sufficient to freeze quicksilver.

XIII. *Single elective affinity illustrated.*—1. Add to the combination of oil with alkali, formed in Experiment X., a little diluted sulphuric acid. The acid will seize the alkali, and set the oil at liberty, which will rise to the top. In this instance, the affinity of alkali for acid is greater than that of alkali for oil. 2. To a dilute solution of hydrochlorate of lime (prepared in Experiment II.), add a little of the solution of pure potassa. The potassa will seize the hydrochloric acid, and the lime will fall down, or be *precipitated.*

XIV. *In some instances, in comparing the affinities of two bodies for a third, a weaker affinity, in one of the two compared, will be found to be compensated by increasing its quantity.*—It is not easy to offer clear and unequivocal examples of this law, and such as the student may submit to the test of experiment. The following, however, may illustrate the proposition sufficiently:—Mingle together, in a mortar, one part of chloride of sodium (common salt) with half a part of red oxide of lead (litharge, or red lead), and add sufficient water to form a thin paste. The oxide of lead, on examining the mixture after twenty-four hours, will be found not to have detached the hydrochloric acid from the soda; for the strong taste of that alkali will not be apparent. Increase the weight of the oxide of lead to three or four times that of the salt; and, after the same interval, the mixture will exhibit, by its taste, marks of uncombined soda. This proves that the larger quantity of the oxide of lead must have detached a considerable portion of hydrochloric acid from the soda, though the oxide has a weaker affinity for that acid than the soda possesses.

Another illustration of the same general principle has been suggested by Berzelius. It is necessary to premise, that the colour of the compound of sulphuric acid with oxide of copper is blue, and that of hydrochloric acid with the same oxide, green. To a saturated solution of sulphate of copper in water, add by degrees concentrated hydrochloric acid. Every addition will render the colour of the liquid more distinctly green, showing an increased production of hydrochlorate of copper; the oxide of copper being divided between the sulphuric and hydrochloric acids, in proportion to the quantity of each acid that is present. In a still greater number of cases, however, a weaker affinity, in one of two bodies compared, cannot be compensated by increasing its quantity. No quantity of tartaric acid, for example, that can be employed, will be found to dislodge sulphuric acid from sulphate of lime.

XV. *Double elective affinity exemplified.*—In a watery solution of sulphate of zinc, immerse a thin sheet of lead: the lead will remain unaltered, as also will the sulphate of zinc, because zinc attracts sulphuric acid more strongly than lead. But let a solution of acetate of lead be mixed with one of sulphate of zinc; the lead will then go over to the sulphuric acid, while the zinc passes to the acetic. The sulphate of lead, being insoluble, will fall down in the state of a white powder; but the acetate of zinc will remain in solution.

CHEMISTRY OF THE IMPONDERABLE AGENTS.

Under this term are usually included, light, heat, actinism, and electricity; a plan which, in deference to common usage, I shall adopt. Probably, however, it might be more consonant with our information to extend the definition in such a manner as to include the causes, whatever they may be, of gravitation, cohesion, and chemical affinity.

It is a pleasing subject for contemplation that, although the facts of science are ever accumulating, yet each new fact serves as a nexus for binding together systems previously disconnected. There is a continual tendency to lessen the number of first causes—a continual tendency to refer manifold results to the operation of fewer great agencies or forces. In this way, viewing the numerous correlations subsisting between magnetism and electricity, it is scarcely permitted to doubt the propriety of referring them to the common operation of one agent. The analogous manifestations of heat and light again render exceedingly probable the hypothesis that these functions are referable to modified operations of the same principle; and the correlations, striking and numerous, subsisting between heat and light on the one hand, and magnetism and electricity on the other, render the nexus of the imponderable agents complete. Passing beyond the limits of this series, there has been discovered by Faraday a striking relation between electricity and chemical affinity; and numerous philosophers have felt themselves justified in assuming a correlation to exist between the functions of cohesion, chemical attraction, and gravitation: hence, it seems not improbable that the numerous imponderable forces affecting matter may hereafter be referred to one operative cause.

Light.—This, as well as the remaining imponderable agents, admits of two distinct kinds of study. We may study it in essence, and in action. Thus, the essence, or condition of light, has been variously appreciated by different philosophers, ancient and modern; some regarding it as a subtle, attenuated matter, to which, for want of a better name, the term ether has been applied; others, as a series of continuous emissions of certain particles, which, by impinging on the retina of the eye, give rise to the impression of luminosity; others, amongst the ancients, as a series of emissions from the eye itself; and yet another class, believing, with Professor Œrsted, that light consists of a series of electric sparks. Such are the chief of the various hypotheses which have been entertained as to the nature of light. Many, if not all of them, involve propositions which may be studied with advantage; but the opinion of philosophers is now divided between two—the corpuscular or emissary theory, and the undulatory or ethereal.

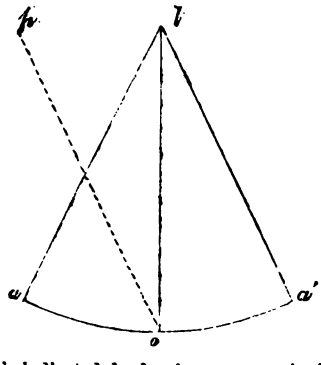
As regards its action, light may be studied with reference to its effects. It may be contemplated as a mere optical agent. Its fundamental properties of reflection, refraction, and polarization,—its effects denominated *chemical*,—its velocity of transmission,—all may be discussed without necessarily adopting any hypothesis concerning its essence or nature; although, as will be found hereafter, the adoption of an hypothesis frequently renders these phenomena more easy of comprehension. There was formerly a prolonged discussion on the question, whether light be or be not material. This discussion has for some time been allowed to rest. Very little consideration suffices to make known, that the appreciation of the term matter will depend upon our definition of it; hence, according as the definition be more narrow or more extended, so will light be regarded as a material, or a non-material agent. Astronomical investigations enable us to judge with great accuracy concerning the velocity with which light

travels through space, being about 192,000 miles in a second of time—a rapidity which, although inconceivable to our comprehension, is, nevertheless, exceeded by the velocity of electricity passing through a copper wire.

The astronomical data on which the velocity of light is calculated are of two kinds; the first being furnished by observations on the eclipses of Jupiter's satellites, the second by observations on the aberration of light. The eclipses of Jupiter's satellites furnish the information required, as follows:—The time when each particular eclipse occurs is accurately known by astronomical investigation; the time when such an eclipse is *seen* to occur is a matter of observation. Now, the diameter of the earth's orbit being 190,000,000 miles, it is evident that our planet is at one time 190,000,000 miles nearer to Jupiter than at another; hence, the visual announcement of an eclipse of one of Jupiter's satellites must, at one period of the earth's revolution—*i.e.*, when the earth is furthest removed—pass through a space 190,000,000 miles greater than when the earth is nearest. Now the time light occupies in passing through this length of space —*i. e.*, 190,000,000 miles (being the length of the earth's diameter)—is about 16 minutes 26 seconds; which gives for the velocity of the passage of light, about 192,000 miles per second. This degree of velocity accords very nearly with that deducible from the phenomenon of the aberration of light, which may be thus explained:—Luminous objects are rendered visible to us by means of light proceeding from them, and acting in straight lines; and the position in space which luminous bodies appear to occupy, is determined by the direction of these lines or rays of light.

As regards celestial luminous objects, our position is continually altering with relation to them; partly, on account of their own motion, but more especially on account of the progressive movement of the earth in its orbit. Now, if light were diffused through space, from any celestial luminous point to the eye, without occupying time, then it follows we should see celestial objects in their real positions for any given time. We do not, however, see them in their real positions, but in positions occupied by them at certain anterior periods, proportionate to the time which light had occupied in travelling from them to the sentient eye. Hence, knowing the real position of a heavenly body at any particular period, and the space the observer travels over in the same time, we have elements for calculating the velocity of light.

For instance, in the accompanying diagram let *l* be a lumious body in space, *a o*, *o á* portions of the earth's orbit travelled over by the observer in some equal time, a second for example. Let *l a*, *l o*, *l á* indicate the direction of luminous rays. It will now follow that *if* light occupy no time in travelling, the luminous object *l* will always be seen in its true position for each time of observation, notwithstanding any progressive motion of the observer. If, on the contrary, light occupy time in travelling, then it will follow that the observer's eye, moving in the direction of *a á*, will never see the luminous body *l*, by virtue of the luminosity emanating at the period of observation; but by virtue of luminosity which emanated at some antecedent period, and the direction or angular position in space of luminous objects is indicated by luminous rays, it follows that *l* can never be seen by an observer



›tion in its true position. When the observer's eye is at *a*, *l* will not appear real position—*i. e.* a position indicated by the direction line *l a*—but in some ›dent position not represented in the diagram. When the observer had arrived the apparent position of *l* would not be indicated by the direction line *l o*, n one corresponding with, *i. e.* parallel to *l a'*, and indicated by the dotted *p*. Now, the distance of a luminous object being known, also its real position :s apparent position, we have the elements furnished for calculating the velocity ht.

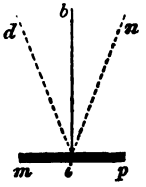
discussing the ordinary optical properties of light, I shall commence with the iation of a few primary laws.

ʃfinition. A ray of light is a rectilinear agency of the luminous essence for any given ıarent medium.—This definition is equivalent with the ordinary expression that travels in straight lines, to the extent that the expression itself is correct. ›ut a limitation, however, as introduced in the definition, the common expression ırrect; the property of travelling or acting in straight lines existing only for an nging transparent medium.

w 1.—The intensity of light varies in an inverse ratio to the square of the distance.

ıat is to say, if the numbers 1 2 3 4 represent four distances from a luminous , then the intensity of light at 2 will only be ¼th its intensity at 1; at 3, $\frac{1}{9}$th; ;t 4, $\frac{1}{16}$th. This can be readily illustrated in the following manner. Let *a* ent a luminous body, 1 an opaque screen, having determinate square dimensions— ›tance, one foot—2 3 4 other opaque screens, having respectively the dimensions), and 16 feet; then at 1, the one-foot screen will intercept all the light at 2, the eet square; and so on for the rest.

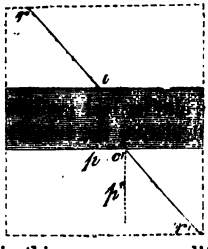
ıw 2.—A ray of incident light being reflected from any polished surface, the nt and reflected rays are in the same plane. Thus, let *m i p* ent a reflective plane, *d* an incident ray, *n* a reflected ray, the point of impact; then the rays *d* and *n* lie in the plane; or, so far as the annexed diagram is concerned, in ane of this paper.



ıw 3.—A reflected ray of light makes equal angles with the nt ray. Thus, in the preceding diagram, where *d i* represents ıcident ray, impinging at *i* and reflected at *n*, the ray *d i* an angle with a line *b i*, perpendicular to the reflecting plane *m i p*, equal to the ade by the reflected ray *i n*.

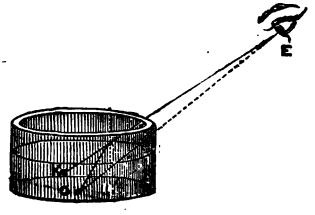
w 4.—When a ray of light passes from one transparent medium into another of r density, it is refracted in a direction towards a perpendicular to the plane of

the refracting surface; when from a transparent medium of greater into one of lesser density, it is refracted from the perpendicular to the plane of the refracting surface.



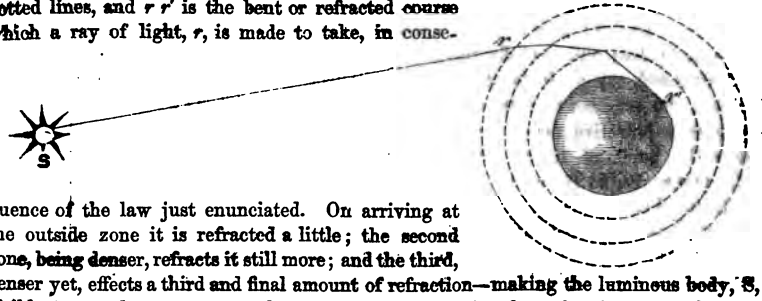
Thus, let the upper dotted rectangular space stand for a refractive medium of atmospheric air, the lower dotted area for the same, and the middle rectangle for a transparent refractive medium, such as glass. Let *r* stand for a ray of light, taking the direction of *r i o r'*. On inspection, it will be found that on entering the glass the ray bends towards the perpendicular *p*, because glass is the denser medium. On leaving it, it bends from *p'* and resumes its original course,—in this manner exemplifying the law.

It is owing to the law of refraction just enunciated, that an object so placed in an empty basin as to be invisible to an observer, on account of the visual ray from it being intercepted by the rim, can be rendered visible by filling the basin with water. The rationale of this will be made evident by the annexed diagram. The object is supposed to be a boy's marble, and it would be invisible by a ray passing in the direction of E K, although visible by the same ray if bent in the direction of O, as would be the case if water were poured into the basin.



For the same reason it is that we never see the heavenly bodies in their true position, even after the slight deviation referable to the aberration of light, and, in certain cases, to parallax, has been allowed for. The atmosphere, far from being homogeneous, continually increases in rarity, as its elevation increases. Hence, the upper regions of the atmosphere are far more attenuated than the lower regions; an attenuation which, although infinitesimally gradual, may, nevertheless, for the purpose of investigation, be contemplated in the sense of diminishing by successive zones, each of uniform density for itself.

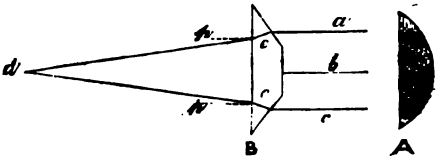
In the diagram, three of these imaginary atmospheric zones are represented by dotted lines, and *r r'* is the bent or refracted course which a ray of light, *r*, is made to take, in consequence of the law just enunciated. On arriving at the outside zone it is refracted a little; the second zone, being denser, refracts it still more; and the third, denser yet, effects a third and final amount of refraction—making the luminous body, S, visible to an observer at *r'*; where, had it not been for the refractive atmosphere, it would have been invisible.



A more common illustration of the refraction of light unequally, by an atmosphere of unequal densities, is afforded by looking at a glowing piece of metal, or a brick-

kiln in action, or the earth's surface in a hot summer day. In consequence of those portions of the atmosphere immediately surrounding these hot objects being rarified, and consequently diminished as to density, their refractive power for rays of light is diminished also, and bodies viewed through them are not seen in their true places. They appear, moreover, to be tremulous, because the hot currents of air rise, and cold ones take their place, thus furnishing a medium of continually varying refractive power.

The theory of lenses directly follows from the operation of the preceding law, as will be recognized after inspecting the following diagram. The simplest mode of seeing clearly the rationale of a lens consists in regarding it, firstly, as having its curves made up of as many small tangent planes as there are rays of light from a luminous body,—that is to say, an infinite number of such planes; secondly, in regarding these planes to be reduced, for the sake of easy comprehension, to a small number. In this diagram, the plano-convex lens A, has been reduced in B to a conventional form, for the sake of exemplification. *a b c* represent three parallel rays of light, each falling on its own plane, going through the lens, and finally converging on the focus *d*. On observing the directive tendency of these rays, with reference to the perpendiculars, *e e*, *p p*, it will be seen that the law is satisfied, and that the natural result of thus satisfying the law is the convergence of the rays *a b c* into a focus. Whatever be the form of a lens, the same law holds good.



Although the mutually variable density of a series of bodies is one cause of variation in their respective amounts of refractive power, yet it is by no means the only cause. Generally, if not always, the combustible tendency of a body bears a direct ratio to its refractive power. Thus, long before the real nature of the diamond was suspected, Sir Isaac Newton advanced the hypothesis that it might be an unctuous substance coagulated, having been led to adopt this opinion in consequence of the diamond's powerfully refractive tendency. Since the time of Newton, his idea, as especially relating to the diamond, has been generalized, and is found to hold good without a known exception.

Hydrogen, phosphorus, diamond, bees-wax, amber, oil of turpentine, camphor, linseed oil, and olive oil, &c., have refractive indices, from two to seven times greater in comparison with their density than most other substances. At one time this law failed to embrace the substance phosphorus, which was described by Dr. Wollaston as having a low refractive power. Sir David Brewster has since demonstrated that, in relation to its density, phosphorus has a refractive power twice that of hydrogen.

The refractive indices of a series of bodies are the ratios of the sines of their respective incident and refractive angles. This ratio, it will be observed, is compounded of the refractive power due to a substance by virtue of its density, and by virtue of another quality. Thus,

Let N = the refractive index, or refractive power, of any substance,

R = the portion of refractive power in such substance proportionate to the function of density,

R′ = the portion of refractive power in such substance proportionate to the function of another quality,

Then $N = R \times R'$.

But it is evident that in any series of refractive substances the mutual ratio of the R′ in such series may be eliminated, for

$$R' = \frac{N}{R}.$$

That is to say, in any series of refractive bodies, the ratio of refractive power not due to density, may be obtained by dividing the number expressing the refractive index of each member by its specific gravity.

Accordingly this has been done in a great number of instances, and with the object of showing that the unknown cause of refraction spoken of above as acting in addition to the cause of density may be the inflammability of a body, understanding in this sense its tendency to combine with oxygen or other electro-negative element,—in other words, the electro-positive quality of the refractive substance.

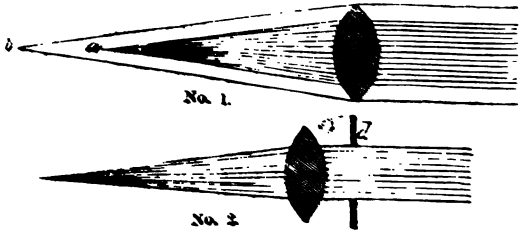
Law 5.—The sine of the angle of incidence and that of the angle of refraction bear a constant ratio for every refractive body of homogeneous density.

Chromatics.—Hitherto light has been considered without reference to colour; the study of this branch of the subject constitutes the science of Chromatics. If a beam of white light be made to impinge on a triangular prism of refracting substance, colour is produced, owing to the decomposition of white light into its components; from which circumstance the deduction may be arrived at that white light is a compound of certain coloured lights, each possessing a given rate of refrangibility. Sir Isaac Newton regarded the coloured rays into which white light might thus be split as seven, as thus arranged, in the order or degree of their refrangibility :—

1. Red	3. Yellow	5. Blue	7. Violet
2. Orange	4. Green	6. Indigo	

and, indeed, no simpler decomposition can be effected by means of the unaided triangular prism. It is, however, now well established that the number of primitive colours in the triangular prismatic spectrum is not seven, but three—namely, red, yellow, and blue.

Spherical and Chromatic Aberration.—Convex lenses, which are segments of spheres, such as the lens No. 1, and those concave lenses, which may be described as planes from which spherical segments have been excavated, may be termed spherical lenses. Such lenses possess the defect of scattering certain rays even of monochromatic light from the true theoretical focus, and producing an indistinct image. This defect is termed spherical aberration. It takes place altogether near the edges of such lenses, and may, therefore, be obviated by means of a curtain, or stop, similar in its nature to the iris of the eye, with its central pupil, although at the expense of a certain amount of illuminative power.



In No. 1 this spherical aberration is represented. The greater number of rays fall, as they ought to do, on the theoretical focus *a*; but a few wander from that point to *b*, and constitute spherical aberration. It will be evident that a diaphragm, or stop, with a central orifice, as represented in section by *d*, will have the effect of cutting off these wandering rays.

The rationale of the peculiar effect which the edges of spherical lenses have in developing spherical aberration, is too purely optical in its character for discussion in this place.

Descartes applied himself to the task of obviating spherical aberration by varying the form of lenses from sections of spheres to sections of certain ovals, which, from the name of Descartes, are termed the Cartesian ovals. He thus succeeded in obviating the defect for any one kind of homogeneous light. In his time the circumstance of the compound nature of white light was not known. Further experience demonstrated that each colour of light possessed its own refractive power; consequently it followed that no lens, however varied as to shape, could be free from spherical aberration as regards white or compound light; or, more properly speaking, what would have been mere spherical aberration with a common spherical lens, became chromatic aberration with a lens formed on the basis of a Cartesian oval.

Chromatic Aberration.—Spherical aberration, we have seen, may take place when mono-chromatic light is employed; but chromatic aberration necessarily presupposes the employment of compound or white light, and is developed like mere spherical aberration by the effect of the edges of spherical lenses on light passing through them.

The rationale of this agency will be easily understood on reflecting that the edges of a lens approach to the character of a triangular prism, the two sides of which adjacent to the edge have been bent into curvilinear forms. The fact, moreover, will be anticipated, that this kind of aberration may be greatly obviated by means of a curtain, iris, or stop. Nevertheless, it is not possible by this means alone to render optical instruments achromatic; and had the optician no better method of obviating the defect than by a stop, refracting telescopes must have remained in the imperfect condition of the time of Sir Isaac Newton; displaying white objects not in their true colour, but surrounded with an iris-like fringe. Newton proclaimed the idea of making achromatic refracting telescopes to be hopeless; nevertheless, it has been fulfilled by a means no less simple than beautiful—the compound lens, the principle of which is as follows:—

Different kinds of glass possess different refractive powers for the same colour of light. Thus, if a glass which may be endowed with the property of refracting yellow and red light by one degree more than blue, be combined with another which has the exactly opposite property of refracting blue by one degree more than yellow and red, then it should theoretically follow that the resulting action of two such glasses should be a perfect compensation. This indeed is found practically to be the case. Perfectly achromatic lenses are now formed of compound glasses placed in apposition; and the achromatic telescope spoken of by the illustrious Newton so despondingly is now amongst the best known and most common of optical instruments.

Before quitting the subject of spherical and chromatic aberration, it is worth while to reflect on the exceeding care which nature has taken against the occurrence of this defect in the eye of man and the higher animals. The provision of the iris, with its central orifice, or pupil, must strike even the most careless observer as being precisely analogous in its nature and functions to the stop or diaphragm of an optical instrument; possessing, however, the beautiful means of adjustment which the optical instrument has not, the power of enlarging or contracting its central aperture to regulate the amount of light admitted. The function of the iris and pupil is evident; but there are other provisions against spherical and chromatic aberration which require dissection to

unfold. Not only is there a stop for the purpose of cutting off wandering rays, but the cornea, the crystalline lens, and the vitreous humour, are none of them spherical lenses. They are formed on the basis of ovals, in order that they may be more effectual in obviating spherical aberration. Nor is this all the refractive power, for one kind of light is different in every one of the transparent lenses and humours of the eye. Nature herself has set the example of compound achromatic lenses, so plainly, so unequivocally, that had the illustrious man who looked so despondingly on refracting telescopes been an anatomist he could scarcely have failed to discover the secret of compound achromatic lenses.

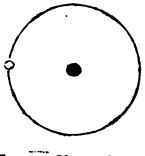
Double Refraction.—The laws of ordinary or single refraction have already been enunciated; but there is also a class of phenomena termed double refraction, which I shall now discuss.

The term double refraction sufficiently indicates its nature. Any object seen through a doubly refracting body in the proper direction appears double; the ray of light being split into two, of which one takes the ordinary course, or very nearly, and is therefore termed the ordinary ray, whilst the other experiences a very remarkable divergence, not only altering its angle but its plane of transmission,—and thus derives the name of extraordinary ray.

The subjects of double refraction and polarization (for they are intimately united) are amongst those which, although remarkably easy in themselves, appear difficult in books, chiefly on account of the difficulty experienced in representing on a flat paper surface, by means of diagrams, actions which occur in two planes at right angles to each other. This, indeed, is the only difficulty attendant on the study of double refraction and polarization, so far as all the more common phenomena are concerned.

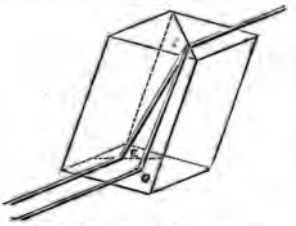
Perhaps the best medium for imprinting first ideas of the nature of double refraction is a rhombohedral crystal of Iceland spar. If such a crystal be taken, and any visible point viewed through it, the image will be reduplicated—provided the crystal be held in all positions but one; which, accordingly, is termed the optic axis of the crystal, also (curiously enough) the *axis of double refraction*. It does seem extraordinary that the term "axis of double refraction" should have been adopted to define the linear direction in which no double refraction takes place. The term, however, has acquired the authority of usage.

If the crystal of Iceland spar be held in such a direction that the two images of an object viewed through it appear, and if the crystal be caused to rotate, then the image resulting from the extraordinary ray will revolve in a circle, whilst the image of the ordinary ray remains fixed. By varying the axis of the visual ray, these two images may be made to assume various distances with regard to each other—distances merging into perfect coincidence when the visual ray corresponds with the optic axis of the crystal, and attaining the farthest limit of divergence when the visual ray is at right angles to the same.



The next experiment which may be performed is as follows:—Let a slice of tourmaline, cut parallel to the crystal's long axis, be taken, and for convenience mounted, by means of a little sealing-wax, on a perforated slice of cork, in such a manner that it may be rotated before the eye. Next set a rhomb of Iceland spar flat upon a piece of paper, on which is marked a single dot at *e*. The dot will be reduplicated (O E), as represented in the following diagram. If now, the crystal

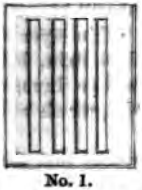
of Iceland spar remaining in this position, the two dots be viewed through the mounted slice of tourmaline, a very extraordinary phenomenon will be noticed. The two dots, although viewed through the same media (the crystal and tourmaline), will appear with different amounts of distinctness. By turning round the tourmaline one image will gradually fade, and the other will grow more evident. By continuing the revolution one will at length altogether disappear, and the other will attain a maximum of conspicuousness. By continuing the revolution the order of phenomena is reversed; that is to say, whichever image was indistinct before will now grow bright, and so the change will alternate,—the same object disappearing at periods coincident with every semi-revolution.



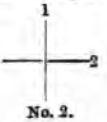
It is quite evident, from the tenour of this simple experiment, that not only has the Iceland spar effected the splitting of one ray into two, but that each ray has become endowed with certain properties,—each ray, to use the ordinary expression, has become *polarized;* hence all doubly refracting substances are also polarizing ones, although the polarization of light may be accomplished also by other means.

In discussing the nature of so subtle an essence as light, it frequently helps the comprehension to illustrate certain phenomena in which it is involved by adopting similitudes. If, then, common or non-polarized light be assimilated to two plane agencies acting rectangularly to each other, as indicated by a rectangular cross +, some consistent basis may be formed for acquiring a knowledge of polarized light in its most simple relations. We have only to assume that a ray formed of these two rectangular agencies, whilst permeating a doubly refracting crystal, gets split into two, and we immediately derive a notion of the properties of double refraction. The reason why the two rays are refracted in different planes is immediately suggested,—and it only remains to frame an hypothesis accounting for the subsequent phenomena observed on viewing the two images through a plate of tourmaline.

If, in regard to this tourmaline plate, we assume it to be endowed with a transmissive property for light, as represented conventionally by the subjoined diagram (No. 1), then our first notions as to the nature of polarized light become very much extended. The reason will be now apparent why only one object produced by a doubly refracting body can be seen in perfection in two positions of rotation, and why each object alternately disappears. Ray No. 1 would only permeate the tourmaline, as represented in diagram (1), so long as its plane might correspond with the direction of the slit-like orifices.



No. 1.



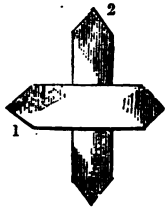
No. 2.

All the phenomena of polarized light harmonize with the general idea of its possessing sides; an idea which was propounded by Newton; but being so extraordinary, was laid aside until Malus, in the year 1810, again drew attention to the subject.

Referring to the experiment just cited of the spar and the tourmaline, it requires now to be indicated that tourmaline is a doubly refractive substance, which accomplishes such a divergence of the rays that one is turned aside or lost. A plate of this kind only admits of the passage of rays in one plane.

All the light which passes through a plane of tourmaline is polarized, as may be

rendered evident by the following simple experiment:—Having provided two plates of tourmaline, each mounted similarly on cork, for convenience of manipulation, let any luminous body, such as a candle, be viewed through one plate, the tourmaline being caused to revolve until a complete circle shall have been described. Next repeat the experiment, using two plates of tourmaline, laid flat together, instead of one. Provided the long axes of the tourmaline plates are coincident, both may be revolved; and the object will, in all phases of revolution of the planes, appear evident as before. No sooner are they placed at right angles to each other, however, than all the light is completely intercepted. When two polarizing agents, such as these tourmaline planes, are employed in conjunction, whether in contact with each other, or some distance removed, the one nearest the eye is termed the analyzing, and the one nearest the object the polarizing plane. These terms will be employed hereafter in reference to another phenomenon. By means of a plane of tourmaline used as an analyzing plane, it follows that the existence of polarized light may be discovered; accordingly, it will presently be assumed to be employed as a means of proving the existence of polarized light arising from another cause.



Double refraction, I have already remarked, is not the only means of effecting the polarization of light,—reflection being also a very usual cause. There is a certain angle at which probably every reflective surface accomplishes the polarization of light. For plate glass, covered on one side with a black pigment, this angle is 57°, and placed at this angle it may be used as a means of effecting polarization. The reflected light may be known to be polarized, either by an analyzing plate of tourmaline, or by another plate of blackened glass held at the polarizing angle, at which an image, if produced by polarized light, will become invisible.

Interference of Polarized Light.—This term, although involving an explanation which will be for some time postponed, must be here mentioned as a means of designating certain brilliant chromatic effects, not less beautiful in themselves than useful, as acquainting us with the molecular constitution of many bodies. Polarized light, therefore, becomes an agent of refined chemical analysis.

If the two tourmaline plates be taken as before, and held face to face—that is to say, in the same plane, but at right angles to each other—a ray of light will be completely intercepted; but if, whilst in this virtually opaque condition, a thin layer of mica be thrust between them, light will be transmitted—no longer white light, but coloured; and on causing the analyzing plate to revolve, these colours will go through all the planes of the prismatic spectrum, except one spot in the middle, which will alternate between white and black.

On attentively reflecting on the bearings of this experiment, it is evident that the interposition of the mica must have depolarized the ray, or, more correctly speaking, must have caused the one plane polarized ray to assume the direction of two planes, being in this respect like common light, but differing from it in the remarkable circumstance, that when viewed by an analyzing medium, it evidences colour.

Before leaving this part of the subject, it is necessary to observe that mica is a doubly refracting substance, belonging to a crystallographic system, characterized by having two optic axes, or lineal directions, through which a ray of light can pass without double refraction. Only doubly refractive bodies yield these beautiful phenomena of colour when treated similarly to mica in the preceding experiments;

hence these coloured rings indicate the existence of double refraction under circumstances in which more direct observation could not be applied.

Nor is this the only amount of information yielded. The spots of alternate white and black which crystalline slices manifest when thus treated, are indicative each of an optic axis, or line of no double refraction; hence the crystalline system to which a substance belongs may, by this means, be determined within very narrow limits. If such a slice do not produce this image under the circumstances mentioned, it does not doubly refract. If it does not doubly refract, it does not belong to the tessular system. If it have only one optic axis, it either belongs to the rhombohedral or right square prismatic systems. If it have two optic axes it belongs to one of the remaining systems, as the subjoined table will render manifest. Before the theory of inter-

TABULAR VIEW OF THE CONNEXION SUBSISTING BETWEEN CRYSTALLINE FORM AND OPTICAL PROPERTIES.

Primary division with reference to symmetry.	Systems or groups of Mohs.	Systems or Groups of Weiss.	Crystallographic axes.	Optic axes. (syn.) axis of double refraction.
Crystals having 3 rectangular equal axes Do not become electrical by heat. Do not expand unequally by heat. Do not doubly refract.	Tessular.	Regular (syn.) cubic octohedral.	3 axes, all rectangular, all equal.	3 optic axes. Do not doubly refract in any position.
Crystals not having 3 rectangular axes Become electrical by heat. Expand unequally by ditto. Doubly refract.	Rhombohedric.	Rhombohedral.	4 axes, 1 rectangular (unequal), 3 intersecting at 60° equal.	1 optic axis. Double refraction in all positions but one.
	Pyramidal.	Right square prismatic.	3 axes, all rectangular, 1 unequl, 2 equal.	
	Prismatic.	Right rectangular ditto.	3 axes, all rectangular, all unequal.	2 optic axes. Double refraction in all positions but two.
		Oblique rectangular ditto.	3 axes, 1 rectangular, 2 oblique, all unequal.	
		Doubly oblique ditto	3 axes, all oblique, all unequal, Symmetry totally wanting.	

ference of polarized light can be adequately discussed, it will be necessary to have offered some remarks concerning the undulatory theory, as being the only one on the assumption of which these beautiful phenomena can be consistently explained. Meantime a few remarks may be offered relative to the connexion existing between these coloured rays and the geometric form of a crystal.

The highest object of chemical philosophy is to unravel the mystery of those great forces with which matter is impressed; to trace their connexions, study their correla-

tions, and read off—so to speak—the hidden energies of one in equivalent functions of another. The study of crystalline form—the investigation of those energies which result in definite mathematical shape—the contemplation of that symmetry between structure and composition which crystals so forcibly display, continually impress the chemical philosopher with the belief, that some great connexions existing between the physical forces will be hereafter made known by a study of crystals—bodies in which all the gauge points of accurate chemistry seem to lie; where the most perfect molecular union is circumscribed by the most perfect geometrical boundaries, and in which the very lines of force to which their construction is due may be brought within the scope of cognisance by means of polarized light.

Corpuscular and Undulatory Theories.—These two theories have been casually indicated. They will now be discussed more fully, inasmuch as a consideration of their tenets will facilitate a comprehension of certain manifestations of polarized light.

The corpuscular theory, although considerably modified by different philosophers, is based on the general assumption that the manifestations of light are due to the impact of certain material particles upon the retina. Accordingly, several attempts were formerly made to weigh those particles, by allowing a ray of light to dart upon the extremity of a delicately-poised balance; and to connect, in other ways, the manifestations of light, with their presumed analogies, amongst the phenomena of ordinary matter. Although no evidence of their weight had ever been obtained, the idea of their material nature was not necessarily abandoned; and the assumption of such particles squared remarkably well with all luminous phenomena, save those of double refraction and polarization. The phenomena of reflection accord so well with an assumption of the corpuscular theory of light, that their most evident analogies can be recognized in the angular measurement included between the line of incidence, and line of reflection, of a billiard ball. The phenomena of common refraction admits of an analogy scarcely less tangible and direct. If a boy's marble be thrown into a tank of water, the marble will not proceed in the direction it would have assumed in an atmospheric medium; but will suffer bending or refraction.

Most of the ordinary phenomena of light involve either reflection or refraction; and most admit of ready comprehension, on the assumption of the molecular theory. The phenomena, however, of what is called interference of light, and the phenomena of polarization, are totally irreconcileable with the tenets of the molecular theory, as the following illustration will make apparent:—

Most persons must have remarked the beautiful series of iridescent colours displayed by certain polished shells. These colours are in no manner connected with the composition of such shells, as may be demonstrated by taking a cast in sealing-wax, when the surface of the cast will also display a similar iridescence. On examining the surface of such shells, or casts taken from them, by a microscope, minute ridges or furrows are discoverable; and to the action of these the phenomena of coloured light is referable. A similar iridescence may be produced by engraving the surface of metals with such microscopic furrows; and, indeed, this process was once applied to a branch of the industrial arts—the manufacture of iridescent waistcoat buttons. In this case the engraved material was steel, and the furrows were made by means of a diamond. The colours thus produced are referred to the action of interference of light, which term involves the theory of undulations, on the assumption of which the phenomenon is easily explicable. It is possible so to arrange the impact of two mono-chromatic

luminous rays against one and the same point, that the two shall either produce an amount of luminosity equal to the combined energies of both, or else perfect darkness, according to the relative distance from the point of impact at which the sources of the two luminous rays are placed. This is what is understood by the interference of light. Two rays of white light are even more susceptible of interference than two rays of coloured light; but in this case the result is colour,—inasmuch as a ray of white light is compounded of three coloured rays, any of which being interfered with, or suppressed, the compound quality resulting in whiteness no longer exists.

On the assumption of molecules, the phenomena of interference are totally inexplicable. It is impossible to conceive the impulsive force of two molecules, each directed to the same point, less than the impulsive force of one—indefinitely less, even to zero, as we must conceive if the theory of molecules be applied to this phenomenon. On the other hand, if we assume the undulatory theory to be true—if we imagine that light is the result of vibrations amongst the particles of an exceedingly attenuated essence—then the phenomena of interference can be readily explained; then we can find the most precise analogies between certain phenomena of light, and of sound, and the curious affections of interference and of polarization become explicable. If on some tranquil day a pebble be thrown into the water of a pond, a series of waves, circular in contour, and gradually expanding, will form. If, whilst these waves are taking their course, another pebble be thrown on the spot where the first impinged, another series of waves will be produced of precisely similar character to the first, and some of which they will overtake. A very familiar result will now be seen. The waves come in contact—but not, to use a scientific term, all in the *same phase of vibration;* at some points two rising crests will coincide, when two waves, by uniting, associate their forces, and, if striking against an object, give a double impact. At other points a rising crest will strike one that is falling; the result of which, supposing the force of each equal, would be the annihilation of both. In this case we are furnished with an example of the interference of aqueous waves. Passing on to the consideration of sonorous waves, it will be discovered that the whole science of musical harmony depends on so adapting the length of these waves that they may coincide in similar phases of vibration. It is well known that if a musical string be divided by a stop into two equal parts, each separate part yields, on vibration, a tone an octave above that of the whole string; it can be demonstrated, moreover, that each half vibrates twice as fast as the whole string—consequently its vibrations must be twice as small. Now it is well known that an octave is the most perfect harmony that can be associated with the fundamental tone—so perfect that the resulting tones blend into one, just as they should do according to theory. Two series of expanding waves—one series double in size to the other—both taking the same direction, must necessarily correspond: there can be no interference.

Inasmuch as the velocity at which sound travels is known, and each particular tone in the musical scale corresponds with a determinate number of undulations in a given tone, the size of sound waves for any particular tone may be calculated, when the number of vibrations for any given tone are known. This has been accomplished by M. Savart by means of a spiked wheel, caused to revolve with known velocities. A known velocity, yielding a known sound, furnishes the required data. It is by an application of the above principle that Professor Wheatestone succeeded in determining the velocity of electricity through a copper wire. Under the head of Electricity the arrangement of Professor Wheatestone will be fully explained.

Let S = *velocity of sound per second,*
N = *number of vibrations per second necessary to produce any given note,*
W = *length of wave corresponding to that note;*

then $\frac{S}{N} = W$.

The velocity of sound in air at mean temperature and pressure is = 1120 *feet in a second. In conformity with the above data, the following table has been constructed:—*

NUMBER OF VIBRATIONS PER SECOND PERFORMED BY WAVES OF AIR CORRESPONDING TO CERTAIN MUSICAL NOTES, AND LENGTH OF THE RESPECTIVE WAVES.

Notes of the organ.	Length of pipe.	No. of vibrations per second.	Length of wave.	
Lowest C	32	16	70	or $\frac{1120}{16}$
C^1	16	32	35	or $\frac{1120}{32}$
C^2	8	64	17·5	or $\frac{1120}{64}$
C^3	4	128	8·75	or $\frac{1120}{128}$
C^4	2	256	4·375	or $\frac{1120}{256}$
C^5	1	512	2·1875	or $\frac{1120}{512}$

These acoustic illustrations have been chosen with the object of facilitating their luminous analogues,—to which I will now return.

If a plano-convex lens be laid with its convexity downwards upon a flat plate of glass, various-coloured rings appear; red manifesting itself nearest the edge of the lens, violet nearest the centre. These colours are due to the interference of light; and whatever be the theory of light adopted, it is evident that a

certain relation between colour and space is manifested in the preceding arrangement, where the lines *a'* and *a*, which I will suppose to correspond with the ring red light, is evidently longer than the line *b'*, which may be supposed to correspond with violet light. Hence these respective lines may be considered as representing the ratio of measurement of the waves, or the particles of light, according to the theory we adopt. Knowing the dimensions of the globe to which such a lens has reference, the measurement of the lines *a b*, &c., admit of calculation; hence we have data of the size of waves (assuming that theory for light) of various colours. The wave of extreme red of the solar spectrum has a length of ·0000266th part of an inch, and vibrates 458 million times in a second. The wave of extreme violet light has a length of ·00000467th part of an inch, accomplishing 727 millions of vibrations in a second. The means of ascertaining the number of vibrations per second of any coloured light are based on the data of the rate of travelling of light per second and the measure of a determinate chromatic wave. An application to these data of the formula given for sound above, making the obvious substitutions, will give the required answer. In order, however, to remove all difficulty from the comprehension of this interesting subject, the following parallel cases have been drawn up:—

PARALLEL CASES.

Light travels at the rate of 190,000 miles per second.	A man travels at the rate of 60 yards per minute.
Length of waves of red light, ·00000266th part of an inch.	(Assumed) length of the man's strides, $1\frac{1}{4}$ yard each.
Query.—How many vibrations does a ray of red light make per second?	*Query.*—How many strides does the man make in a minute?
Formula for solving the query.	*Formula for solving the query.*
$\frac{\text{Velocity of light per sec.}}{\text{Length of wave of every colour}} = \text{No. of vibrations per sec.}$	$\frac{\text{Velocity of man per min.}}{\text{Length of stride}} = \text{No. of strides per min.}$
Or,	Or,
0·0000266)190,000(458 millions of vibrations per second. (Answer.)	$1\frac{1}{4}$)60(40 strides per minute. (Answer.)

Interference of Polarized Light.—Having offered a general indication of the nature of luminous interference, let us now apply the facts deduced to an explanation of a phenomenon already indicated,—the occurrence of chromatic rings on interposing a plate of mica between two plates of tourmaline. Plate No. 1,* or the polarizing plate, effects polarization of a ray of white light, so that plate No. 2, the analyzing plate, held transversely to the first, intercepts the polarized ray. A film of mica interposed between, causes the ray again to appear, but as a coloured ray.

It is, in the first place, evident that the mica must have turned the polarized ray partly round, in order that the second plate of tourmaline could have admitted of its passage at all; and it is assumed rationally enough, on the assumption of waves, that in this act of turning round, the various-coloured rays assume different planes, so that, on separating these planes, and rendering one alone evident by an analyzing plate, colour results. A plate of any crystalline body (not belonging to the tessular system) thus introduced between two polarizing media, yields colour, and the optic axes of a crystal may be counted off. It is consistent with reason to suppose that these optic axes correspond with real directions of forces in equilibrio; and it might be inferred that homogeneous non-crystalline transparent bodies would not produce this effect on polarized light; which is again consistent with all observation. If a piece of well annealed glass be interposed, no colour results, because the force holding its particles together is equal in all directions; if, however, the same glass be compressed by means of a hand-vice, or caused to expand unequally by holding a hot poker near it, then iridescent hues immediately appear.

Hence arises an easily applied test of the homogeneity of glass—a quality so necessary for all optical purposes.

Circular Polarization.—Many specimens of rock crystal may be selected which, if sliced, and the slice placed, as directed, between a polarizing and analyzing plate, do not yield the alternating black and white central spot and radiating cross; but instead of which, the central spot is chromatically illuminated, with a colour that changes through all the prismatic series on causing the quartz plate to revolve on its own axis. In some specimens of quartz, rotation of the plate on its own axis from right to left

* See page 76.

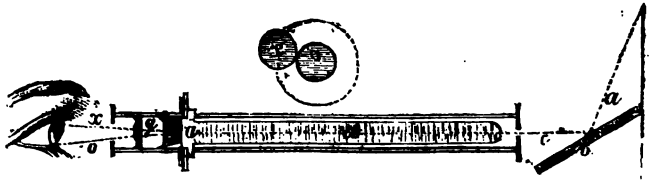
causes the colours to appear in the order of red, yellow, blue; whereas, in other specimens of quartz, this order of alternation occurs when the quartz is turned in an opposite direction. Hence there is right-handed quartz (the former), and left-handed quartz (the latter). This quality of circular polarization is another powerful agent of chemical analysis. On first contemplation it might be supposed to be connected with the solid molecular condition of the crystal; but this is not so—the property of circular polarization being also affected by certain liquids.

The subject of circular polarization is one strikingly illustrative of the way in which a subject apparently altogether abstract and recondite may be applied to the most practical ends. Two remarkable examples of this application I shall mention—the first relating to a method of indicating the progressive change during fermentation of starch into glucose or grape-sugar; the second relating to a method of distinguishing between the latter in glucose and sugar of the cane.

When infusion of malt is mixed with yeast, and exposed to the proper fermentative temperature, a gradual change takes place of starch, and a modification of starch, called dextrine, into the glucose or sugar of grapes, to which the sweetness of the wort is due. Now, solutions of starch, and dextrine, and grape-sugar, all possess the property of circular polarization; but with this difference,—the two former polarize towards the right (whence the name dextrine is derived), the latter polarizes towards the left. Hence, by placing an infusion of malt, at progressive stages of fermentation, in a tube of definite length, connected with a polarizing apparatus, and reading off the amount of right-handedness or left-handedness displayed by the solution, the progressive changes of starch and dextrine towards grape-sugar or glucose may be made evident.

Still more important is the application of this principle to the discrimination of cane and grape sugars. Slightly anticipating the subject of organic chemistry, it must be here premised that the terms glucose or grape-sugar are not specific, but generic; they are not limited to the indication of sugar which is contained in the grape, but extend to the comprehension of all sugar, from whatever source, having an identical composition. In like manner, by the term cane-sugar we understand a sugar, from whatever source derived, that has a composition of the saccharine crystals extracted from sugar-cane.

Cane-sugar is that alone which possesses any value as a manufactured article; the only kind which admits of crystallisation or formation into loaves. Yet cane-sugar rapidly, under certain circumstances, changes into grape-sugar; and as both yield a solution, sweet, colourless, and probably of equal specific gravities, the value of a process for determining the presence and the proximate amount of either becomes of the highest importance. By taking advantage of the fact that cane-sugar polarizes circularly towards the right, grape-sugar towards the left, the necessary information can be obtained.



M. Biot has contrived an optical instrument for this specific purpose. Its form is represented by the accompanying diagram.

A ray of common light having been polarized by reflection at the angle of 56° 45′ from the surface (*b*) of a plate of glass, the plane polarized ray (*e*), obtained by this means, is first made to pass through a lens (*g*) to give distinctness of image, and then through a pure solution of crystallizable cane-sugar (*d*): the emergent ray (*e*) being now analyzed by a double refracting rhomb of calcareous spar (*f*), two coloured images are perceived, one (*o*) caused by ordinary, the other (*x*) by extraordinary refraction. The colours of the two images are complementary; that is, when one image is red, yellow, or blue, the other image is green, violet, or orange. If, now, the analyzing rhomb of calcareous spar be rotated, change of colour is effected. If the rotation be right-handed—*i. e.*, in the direction of turning an ordinary screw—the colours follow each other in the order of red, orange, yellow, green, blue, indigo, and violet; meantime, the extraordinary image assumes a series of complementary tints. But the chromatic relation of the two images may be most readily perceived by the following comparative arrangement:—

ORDINARY IMAGE.	EXTRAORDINARY IMAGE.
Red	Green
Orange	Blue
Yellow	Indigo
Green	Violet
Blue	Red
Indigo	Orange
Violet	Yellow
Red	Green

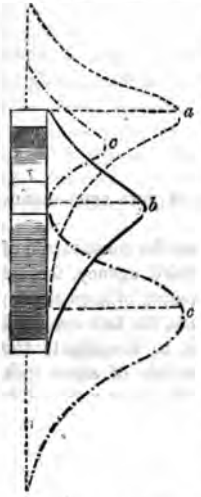
Such is the sequence when the instrument contains a solution of pure cane-sugar; if grape-sugar be substituted, the order of sequence is reversed.

Actinism, or Tithonicity.—Until within the last few years the constituents of the solar rays were supposed to be merely light and heat: a third agency, termed actinism, is now recognised. "The alchemists observed the blackening of horn-silver; but as this discovery did not generate a correct idea in their minds, the fact remained valueless to man. Scheele, the Swedish chemist, was the first to investigate the peculiar conditions under which this remarkable change of chloride of silver took place, and determined the difference in the action of the least and the most refrangible spectral rays. Berard afterwards proved that the most luminous of the prismatic rays would not, even when concentrated by a lens, blacken chloride of silver in twenty minutes; whereas the least luminous rays at the most refrangible end of the spectrum, condensed in the same manner, produced a great degree of darkness on this salt in a few seconds. In 1803, Wedgwood, the porcelain manufacturer of Etruria, employed this chloride and the nitrate of silver, spread on paper and white leather, for copying the coloured glass pictures in church windows; but he failed to give permanence to the impressions he produced. Between 1814 and 1827, M. Niepce, of Châlons-sur-Saône, was employed in investigating this subject, and discovered that resin spread on metallic or glass tablets was sensitive to solar agency, the parts exposed becoming more soluble than those in shadow. By this means he was enabled to produce pictures upon silver tablets by the use of the camera obscura. Niepce, in 1829, associated himself with Daguerre, who had previously commenced some independent observations; and

their combined experiments led to the discovery of the process known as the Daguerreotype, which was published in 1839.

"Mr. Henry Fox Talbot had been engaged in experiments on the chemical agency of the sunlight from 1834; and, in 1839, he first published his photographic researches, and circulated specimens of his process of preparing pictures upon paper covered with chloride of silver. This led to numerous investigations; and several processes, by Sir John Herschel and others, were speedily published. In 1841, Mr. Talbot published—having previously patented—his calotype process; since which time the art has made rapid advances."—HUNT.

Even so far back as the year 1801, Ritter, of Jena, made the important discovery, whilst repeating the experiments of Scheele, that on throwing the prismatic spectrum on a sheet of paper impregnated with chloride of silver, that not only was the blackening, or chemical effect, more powerful at the violet end of the spectrum than at the red, but that the effect was greatest of all beyond the limits of the violet, consequently beyond the luminous boundary of the spectrum. This discovery soon gave rise to the idea that some agency distinct from heat, on the one hand, and light on the other, must exist in the radiant spectrum. Almost contemporaneous with the discovery by Ritter of the existence of what is now termed actinism, Dr., afterwards Sir William, Herschel was prosecuting a course of experiments to manifest the distinction in the prismatic spectrum between rays of heat and mere luminosity. In the year 1800, whilst making some experiments on coloured glasses, intended for the purpose of defending his eyes from heat whilst examining the sun with his large telescope, he found that a deep red glass, notwithstanding its obstruction of a large amount of light, scarcely, if at all, interfered with the passage of heat. On the other hand, a blue or gray glass defended his eye completely. On looking more narrowly into this subject, Herschel proved for heat what Ritter had previously done for actinism, that not only of all the coloured portions of the spectrum did red afford the greatest amount of heat, but the maximum point of spectral heat was developed altogether beyond the red. Thus, it seems, the decomposition of radiant matter by the prism may be indicated, as in the accompanying diagram, where the three recognizable effects of heat, light, and actinism, or chemical power, are represented by three distinct but mutually intersecting series of waves.



It will be observed, from an examination of this diagram, that whilst heat (*a*) and light (*b*) have each one point of concentration, actinism (*c*) has two. Examination of the spectral chart, as the foregoing diagram may be termed, will also tend to create the supposition, which certain practical observations go to confirm, that the three qualities of light, heat, and actinism, are mutually antagonistic of each other. So far as concerns light and actinism, M. Claudet has proved (Phil. Trans., 1847) that yellow, the point of greatest light, is not only negative, but positively destructive, to actinic power.

The subject of actinic radiation is of especial interest in connexion with the art of

Heliography, or the taking of sun pictures, most improperly, as Mr. Hunt observes, termed Photography—a term indicative of the agency of light, whereas we have made it appear that not light, but a peculiar radiant matter, or essence, accompanying light is the cause of the result in question. These sun-pictures may be chiefly arranged under the heads of Daguerreotype and Calotype, although other processes for developing them have been described under the names of Fluorotype, Ferrotype, Chromotype, Chrysotype, Cyanotype, Catalisotype, and Anthotype. All these terms have reference to the chemical agents with which sun-pictures are produced. It will be convenient to discuss the subject here under the two general heads of simple pictures, or those generated without lenses, and camera pictures, in the development of which lenses arranged in the camera obscura are employed.

Simple Pictures.—The process adopted by Wedgwood for copying the paintings on church windows resulted in the formation of a simple photographic picture. However that process may be modified, the principles involved in taking and rendering permanent this class of pictures are invariable.

1. The first condition is the generation of a surface which shall be sensitive to actinism.

2. The second, that the sensitive surface thus developed shall be placed under the unequal action of actinic rays.

3. The third, that the picture shall be fixed.

Sensitive Paper.—Although silver salts are not the *only* substances employed for the purpose of making sensitive paper, yet they are the most usual and most important. It will be well, therefore, to describe the principles on which their successful action depends.

Pure nitrate, bromide, iodide, or chloride of silver, are not affected—that is to say, do not blacken under the influence of actinic rays; but the presence of a little organic matter renders them very prone to undergo this change. Hence, if organic matter, such as paper, or linen, be moistened with nitrate of silver solution, and exposed to the air, the tissue thus acted upon soon turns black on exposure to the solar rays. On this principle depends the operation of marking-ink.

Nitrate Paper.—The most original and most simple kind of sensitive paper for simple pictures is made by brushing over a piece of highly glazed paper a solution of nitrate of silver, containing about 100 grains of the crystallized salt to one ounce of water, and allowing the paper to dry. By this operation a sensitive surface is produced, on which the figures of objects may be developed by very obvious means. Suppose, for instance, it were desired to take copies of the wheels of a watch, nothing more would be necessary than to lay them flat on such a paper, and expose the whole to the action of solar rays. Wherever the rays might strike, the paper would become blackened; but it would remain white in all those portions covered by the wheels. In like manner, supposing it were desired to copy an engraving, or to take the pattern of lace, of a fern frond, of a leaf, &c., nothing more would be requisite than to press the object to be copied and the sensitive paper flat between two glass plates, and to expose the whole to the sun's rays.

By the proceedings described we should obtain a negative picture—that is to say, the lights and shades would be reversed—for a very obvious reason. Just as obvious is it that a positive picture might be made, by exposing the negative one to solar action in contact with another sheet of sensitive paper.

But whether the picture be positive or negative, it is evidently necessary to bring

it to such a condition, that when removed from the object copied the white portions shall be rendered insensible to the solar rays. This operation involves the employment of some chemical agent which has the power of dissolving away such portions of the silver salt, or other agent used, as may not have been affected by the actinic rays. For the paper described, the fixing agent may be a solution of common salt, which has the property of changing all nitrate still remaining undecomposed into a chloride, and of dissolving the latter; a solution of hyposulphite of soda, however, is more generally employed.

Chloride of Silver Paper.—This is made by first washing over the surface of paper a solution of common salt, then with a solution of nitrate of silver. The best proportions of materials are 60 grains of common salt to 3 ounces of water; and 60 grains of nitrate of silver to 1 ounce of water. The application of these and other solutions employed in photographic manipulations, requires much delicacy of hand. The great object in all cases is to effect an even distribution. Brushes, for the most part, are ineligible, not only on account of their rapid destruction by the substances with which they come into contact, but also on account of the great difficulty experienced in laying on a perfectly flat coating of liquid by their means.

A plan very much had recourse to by photographers for distributing their liquids is termed *floating*, and consists in laying the paper, or other substance to be treated, flat on the surface of the liquid, placed in a shallow porcelain or glass dish,—or even on a flat plate of glass, accurately adjusted to a level; then drawing the paper off, and causing it, during this operation, to come in contact with the edge of the dish or plate, so that the necessary amount of superfluous fluid may be removed.

Another good plan consists in laying the paper flat on a glass plate, then pouring upon it a certain superfluity of liquid, and passing the latter evenly over the surface of the paper by means of a glass rod held evenly and horizontally; this plan, however, is restricted to operations which involve the use of paper already wet.

Whatever the mode determined on for spreading photographic solutions, every care should be taken to spread them evenly. If an unwetted patch or spot be recognized, the operator should not fill it in, but should begin the operation of distribution over the whole surface again. Chloride of silver paper which has been prepared as described should be allowed to dry in the dark; when dry, it is ready for use.

The proportions of nitrate of silver and common salt just given may be varied, within certain limits; and a variation in the amount of sensitiveness, and also in the tone of the picture, results. If the chloride of sodium be in excess, the paper will not be very sensitive, and the resulting picture will have a somewhat disagreeable slate colour. Quantities successively lessening give black, bronze, and brown, of various shades, gradually ending in brick-red.

Bromide Paper.—60 grains of bromide of potassium having been dissolved in 3 ounces of water, paper is to be soaked in this,—superfluous moisture absorbed by bibulous paper,—then covered on the surface with a solution of nitrate of silver and water, 100 grains of the salt to an ounce of water.

Ammonia-nitrate of Silver Paper.—If liquor ammoniæ be added to a solution of nitrate of silver, nitrate of ammonia results, and oxide of silver is deposited. If still more ammonia be added, the oxide of silver re-dissolves. Correctly speaking, the so-called ammonia-nitrate of silver, is a solution of oxide of silver in liquor ammoniæ, mixed with a portion of nitrate of ammonia. Very good proportions for making this solution are, 30 grains of nitrate of silver, dissolved in 1 ounce of water, and sufficient

ammonia not only to precipitate the oxide of silver, but to re-dissolve the greatest portion of it,—a trifling amount being left undissolved, for the purpose of assuring the operator that the amount of ammonia added has not been in excess.

The solution as thus prepared is, as I before remarked, a mixture of oxide of silver dissolved in ammonia, with nitrate of ammonia. The presence of the latter is considered objectionable by some photographers, inasmuch as it imparts to the resulting pictures a deep red tone. This effect may be obviated by carefully removing all the nitrate of ammonia solution, so that only a solution of oxide of silver in ammonia shall remain. The steps for accomplishing this end are as follow :—Add solution of ammonia to the nitrate solution, so long as any precipitate forms. Decant the supernatant liquor (which is a solution of nitrate of ammonia),—wash the oxide well with distilled water,—pour off the latter,—then add ammonia, and effect the solution of the oxide as before.

Paper prepared with the ammonia-nitrate of silver is sensitive without any other treatment; but certain artistic effects may be produced by not using it until it has been treated with bromide, chloride, or iodide of potassium, as I have already described. Whatever be the kind of sensitive paper employed, it is absolutely necessary that the engraving, leaf, &c., to be copied, should be pressed firmly down upon it. This is accomplished by an instrument termed a pressure frame. When the subject to be copied is of even thickness throughout—such as an engraving on paper—the adjustment is so easily effected as to require no explanation. When, however, the subject is of uneven thickness—such, for instance, as a leaf with its thick midrib and ramifying nervures—the case is different. Occasionally, it will be desirable to shave down the more prominent portions of the midrib, by means of a penknife, and the object may be afterwards pressed close to the glass by putting a thick piece of flannel in the pressure-frame, below the paper.

The Positive Picture.—The method of obtaining a positive from a negative picture has already been indicated. Occasionally the process will be facilitated by rendering the negative, or object to be copied, more transparent than natural, by means of oil, varnish, or melted wax. In using these agents, however, care should be taken not to impart a shade of yellow to the negative. Yellow, as I have already indicated, is a great impediment to the development of actinic images, over which it exerts a direct negative influence.

Fixing.—In order that a photographic representation may be permanent, it must be "fixed"—to use the technical expression—that is to say, it must have all the silver which has not been converted into oxide or metallic silver by the actinic rays removed.

Fixing is accomplished by the employment of some solvent that has the property of combining with the undecomposed silver salt. The solvent now generally used is hyposulphite of soda, in aqueous solution.

The operation of fixing is commenced by immersing the picture in a dish of hot water, and pouring away the latter, by which means the nitrate of silver, and other salts soluble in water, are removed. The picture should now be dried between folds of bibulous paper, returned to the washing dish, and treated with an aqueous solution of hyposulphite of silver, having the strength of about 120 grains to a part of water. Finally, the picture should be removed from its hyposulphite situation, put into cold water, and washed until a drop of the fluid let fall upon a plate of glass and evaporated leaves no stain.

Positive Pictures on Albuminous Surfaces, on Films of Collodion &c.—The various inequalities of paper present such an impediment to the photographic art that many schemes have been proposed, and some carried into successful execution, for developing positive pictures on smoother substitutes. Of these, a coating of albumen, spread on paper or glass, or of collodion—*i. e.*, solution in ether of gun cotton upon the same—are the principal. Details of these processes scarcely come within the scope of a treatise on general chemistry. I must, therefore, refer the reader who would prosecute the subject of Heliography more minutely, to books specially written on the subject.

Camera Pictures.—Under this description are included the delineation of forms on paper, albumen, &c., in consequence of the decomposing effects of solar rays on certain metallic solutions—comprehending the operations termed Calotype, Talbotype, Cyanotype, &c.; and the delineation of images on an iodized silver plate, known as the Daguerrotype.

If any of the sensitive papers already described be placed in the camera obscura, and the image of an illuminated object allowed to impinge upon it, a picture will in the end result. The time, however, necessary for the development of this picture—usually some hours—is a great bar to the employment of this means of taking actinic pictures.

To Mr. Fox Talbot is attributable the discovery of a process by which the time of the operation is abridged from hours to seconds; and thus a new development of heliography has sprung up, known under the name of Calotype, or, in compliment to its discoverer, Talbotype.

It has been already casually remarked, that pure bromide, iodide, and chloride of silver, are very little, if at all, affected by the sun's rays; but that the presence of a slight amount of organic matter causes the affection to occur readily. This circumstance lies at the foundation of the process of Mr. Fox Talbot; although it is only fair to state that the fact had been anticipated by Sir John Herschel and Mr. Robert Hunt, gentlemen to whom the interesting art of heliography is so much indebted.

The operation of rendering paper suitable for taking Calotypic impressions consists of two processes; of which the first consists in impregnating the paper with certain silver salts,—the second, in rendering the paper so treated additionally sensitive.

Impregnation of the Paper.—Several processes are recommended for this purpose: the following answers perfectly well:—Having dissolved about twenty grains of crystallized nitrate of silver in an ounce of distilled water, precipitate it by the cautious addition of iodide of potassium. The supernatant liquid, which contains nitrate of potash, is to be poured off, inasmuch as that salt interferes with the beauty of the picture. The precipitate, which is iodide of silver, is now to be dissolved in a solution of iodide of potassium, containing fifty grains of the salt to an ounce of water. The paper is to be washed over with this solution, dried, then washed in distilled water, and dried again. This last washing has the effect of precipitating iodide of silver in the texture of the paper; because, although soluble in strong solution of iodide of potassium, it is insoluble in a weak solution of the same. Hence the final process of washing, by converting a strong into a weak solution, precipitates the iodide.

Rendering the Paper Sensitive.—The process depends upon the fact made known by Sir J. Herschel and Mr. Robert Hunt, that organic matter promotes the solar decomposition of certain silver salts. It consists in applying to the paper, already iodized as described, a solution of gallic acid and nitrate of silver mixed together, along with some acetic acid. The following proportions are taken from an excellent little

work, by Mr. Bingham, on Photographic manipulation:—"Dissolve 100 grains of crystallized nitrate of silver in two ounces of distilled water, to which add one-sixth of its volume of strong acetic acid (which will be two and two-thirds of a drachm): this solution should be kept in a bottle excluded from the light. Now make a saturated solution of gallic acid in cold distilled water,—the quantity dissolved is very small. When some paper is to be prepared, five drops of each should be mixed with one ounce of distilled water, and then poured upon the plate-glass, having adjusted it by the set screws so that the solution will not run off; the sheet of iodized paper should then be carefully applied to the wet surface, and the air-bubbles gently pressed out by passing the finger over the back of the paper. As soon as the paper has ceased to curl upwards it should be removed from the glass, very gently pressed between folds of blotting-paper—but only just enough to remove any shining patches of moisture on the surface—and then placed at once in the frame of the camera."

Developing the Picture.—Having caused the image of any object to fall, by means of a camera, upon a piece of paper treated as already described, a corresponding heliographic image will be impressed, although not visible until developed. This development is effected by exposing the invisible picture once more to the action of gallo-nitrate of silver, then exposing it to a gentle heat, such as that produced by a jet of steam.

The best means of distributing the gallo-nitrate evenly over the paper's surface is by means of floating, as already described, the solution of gallo-nitrate being distributed over a glass plate, or poured into a shallow dish, and the active face of the paper superimposed upon it. Immediately the picture has become developed it should be fixed, by means of the process already described at page 87.

Pictures on Metallic Plates—The Daguerreotype.—The history of Daguerreotype is comprehended in the history of heliographic representation generally: hence I have already given a slight account of it. It now remains to offer an outline of the process adopted for producing these pictures in modern practice.

In the heliographic operations already described, the image is impressed upon a non-metallic surface, usually paper, either impregnated or covered with the sensitive material. In the Daguerreotype operation a plate of silver is employed as the recipient of the impression, or, more properly speaking, a layer of iodide or bromide of silver, either singly or mixed, generated by exposing the plate to the operation of these agents.

Thus treated, the silver plate becomes extraordinarily sensitive to light; and if placed in a camera obscura, under the proper conditions, an invisible picture is impressed upon it, capable of becoming an evident picture when the proper developing influence is applied.

The developing agent for heliographic representations of this class is mercurial vapour, which, by means of an agency still very obscure, brings out the picture. At this stage, however, the representation is very easily rubbed off; consequently some preservative means is necessary, that most usual being a deposition of a layer of pure gold over the whole face of the picture—a layer thin enough to be transparent—thin enough to protect the Daguerreotype image from any mechanical casualties to which it may be exposed.

Simple though the various operations connected with the Daguerreotype may appear, they all require much practice for their successful accomplishment.

The first step of the operation consists in obtaining the silver surface to be operated upon perfectly clean, but at the same time without scratches. This is usually accom-

plished by exposing them to the friction of rubbers or buffers of cotton velvet or doeskin, charged with oil and rotten-stone, tripoli, &c., in the first case, and finally uncharged with any extraneous substance.

It is absolutely essential that the Daguerreotype plate shall be free from scratches; not less essential is it that no oil should remain. Hence, whatever care may have been taken in polishing the plate by the dry buffer, it is generally necessary to remove every lingering trace of oil by the operation of burning, as it is called; *i. e.*, the plate being held over a spirit lamp flame, all remaining traces of oil are, by the heat thus applied, decomposed.

This process of burning is one of considerable delicacy. If carried too far, or not far enough, the picture is damaged. Nothing but practical experience can assure the operator that he has made the proper compromise.

As regards the methods of applying friction to Daguerreotype plates, they are very numerous. In large establishments the surface of friction is frequently a circular buffer, vertically revolving, against the flat side of which the plates are pressed. Amateurs content themselves with some form of manual operation; and, indeed, whatever variety of polishing apparatus may be used in the first stages, the last, technically called "laying the grain," must be effected by hand. It consists in rubbing the surface of the plate in *one direction*, by means of a buffer, something in the shape of a brush.

Rendering the Plate Sensitive.—The original agent employed by M. Daguerre for this purpose was iodine vapour; but the amount of sensitiveness thus communicated was very slight in comparison with that resulting from many of the compound agents now employed.

M. Claudet, to whose philosophic investigations the art of heliography is so much indebted, was the first to notice that a silver plate, which had already been iodized, might be rendered still more sensitive by exposure to the action of chlorine. Other investigations soon proved that bromine effected a still greater susceptibility. In consequence of these discoveries, iodine is at this time never used alone as the sensitive agent. It is either combined with chlorine or bromine; and the compound vapours are either used at once, or the different vapours are employed successively.

Method of Applying the Sensitive Vapour.—Whatever be the vapour employed for the purpose of rendering a Daguerreotype plate sensitive, the usual plan of application is as follows:—The solution, or other material from which vapour is to be evolved, being placed in a glass or porcelain dish, the metallic plate to be acted upon is attached to the cover of the dish, and inverted over the vapour, until, on removing the plate from time to time, certain conventional tints appear; guided by these the operator knows when the process has been carried to a sufficient extent. On the supposition that the process of rendering sensitive is conducted by successive operations, of which iodizing is the first, the following details will be applicable.

Iodizing.—A few crystals of iodine being evenly distributed over the bottom of the pan, the plate to be affected is to be attached to the cover, and superimposed. The iodine vapour will now rise, attach itself to the silver, and produce various successive tints in the following order:—

Pale yellow,
Deep yellow,
Blood red,
Rose colour,
Blue.

The colour now seemingly disappears, although in reality the plate becomes yellow again; and by continuing the operation, the chromatic series will be repeated in its former order. If iodine is to be the only sensitive agent employed, then the second yellow corresponds with the most sensitive epoch; therefore, on observing this colour the plate should be removed. If, however, as is now usual, some additional sensitive agent has to be applied, the operator is allowed a far wider range of colour to select from. The epoch corresponding with either colour of the series may be selected; but each requires its own corresponding tint to be developed in the next operation.

Acceleration of Sensitiveness—Bromine.—A plate already exposed to the vapour of iodine has its sensitiveness much increased by subsequently acting upon it by means of bromine. The most usual plan of employing this agent consists in obtaining an aqueous solution; to the vapour arising from which the plate is exposed.

"Bromine water," as it is technically called in the language of Daguerreotypic art, is produced as follows:—

First make a saturated aqueous solution of bromine, by dropping some of this body into water, agitating, allowing subsidence to take place, and finally decanting all the water which remains floating above the yet undissolved bromine. One part of this solution added to forty parts of distilled water constitutes the bromine water, of which the vapour is employed, by exposing the already iodized plate to it in a vessel similar to that already employed in the iodising process. According to Mr. Bingham, there is a corresponding tint with bromine vapour for every tint already developed with iodine, and at which the maximum amount of successful effect will be developed. A tabular view of these tints has been drawn up by this gentleman, and which is here appended.

1st. Iodine.	Bromine.	2nd. Iodine.
Straw Colour.	Yellow.	Full Yellow.
Light Yellow.	Golden Yellow.	Rose.
Golden Yellow.	Light Rose.	Deep Rose.
Blood Red.	Damask Rose.	Light Blue.
Damask Rose.	Deep Rose.	Blue.
Deep Rose.	Light Blue.	Indication of Second Yellow.

This table is drawn up in anticipation of the third process of development, not yet mentioned, and which consists in submitting the plate once more to the agency of iodine vapour.

Instead of using the bromine and iodine separately, they may be combined, and the process of rendering the plate sensitive concluded at one operation.

Solid Sensitive Agents.—A great disadvantage attending the employment of aqueous solutions in Daguerreotype operations arises from the aqueous vapour which continually deposits upon the metallic plate. In order to obviate this, certain English Daguerreotypists have recommended the use of what are ordinarily termed bromide and iodide of lime respectively—compounds formed by bringing hydrate of lime into direct contact with bromine or iodine, and which are the analogues to the so-called "chloride of lime." These compounds answer perfectly well, and are exclusively used by some of our most successful operators.

Impression of the Image.—After the plate has been rendered sensitive by either of the methods already described, it is in a condition for the image to be impressed. This is accomplished by placing it in the camera, and allowing the desired image to be projected upon it for a sufficient time, which depends upon many circumstances, such as the power of sensitiveness acquired, the latitude, time of the year, time of the day, and colour of the object to be represented. Twelve seconds may be, however, regarded as a medium.

Mercurialization.—When the plate is removed from the camera, no image will be visible, although impressed. It is developed by exposing the plate to vapour of mercury, generated at a temperature not exceeding 200°; by preference, at a temperature of 150°.

The apparatus for conducting this operation has been variously modified to suit the taste of different operators: in principle, however, it is exceedingly simple, merely consisting of a chamber, on the floor of which a little mercury is deposited, and heat applied externally, until the desired temperature (known by a thermometer, the bulb of which sinks into the mercury, and the stem of which appears externally) has been acquired.

Removing the Excess of Sensitive Coating.—As soon as the development of the picture has been completed, the excess of sensitive coating remaining upon it must be removed, which is accomplished by washing it with an aqueous solution of hyposulphite of soda, and finally with distilled water. The proper strength of the hyposulphite solution is one ounce of the salt to a pint of water. The process is conducted by plunging the plate, face upwards, into the solution, already poured into a porcelain dish; then removing it, and finally washing with distilled water.

Gilding the Plate.—There are two plans of accomplishing this—either by means of the hyposulphite of gold, or by a mixture of chloride of gold and hyposulphite of soda. The usual strength of hyposulphite of gold is fifteen grains to a pint or water. If hyposulphite of soda and chloride of gold be used, the solution is to be prepared as follows:—

Dissolve 15 grains of crystallized chloride of gold in a pint of distilled water, and 45 grains of hyposulphite of soda in another pint; next incorporate the mixtures gradually by pouring the chloride into the hyposulphite. The operation of gilding is conducted by placing the plate flat, and pouring upon the impressed face sufficient of the liquid to cover it. The flame of a spirit-lamp is now very cautiously applied underneath. Presently the image will turn blackish; but gradually recovering its lustre, will become far more brilliant than before. It is now to be seized at one corner by means of a pair of pliers, washed with distilled water, and carefully dried. The safest plan of drying consists in dipping the plate into hot distilled water, suddenly removing it, and promoting evaporation by blowing upon its surface.

General Chemical Effects of Non-Calorific Radiant Matter.—The subjects of Calotype and Daguerreotype have been enlarged upon because of their practical importance, rather than in consequence of their affording any precise indications of their immediate cause. To aver that these phenomena are dependent upon some chemical agency, manifested by the sunbeam, is only to express a fact.

I shall conclude the subject by noticing a few of the instances in which the solar rays affect chemical decomposition.

It is well known to gardeners and agriculturists that growing vegetables require to be exposed to light. Most probably, the expression should be modified to "actinism," or

"tithonicity." Vegetables which grow in darkness are never vigorous; more or less, their natural secretions are modified, and their colour altered; their structure, too, is watery. Under those circumstances, they do not appear to have been able to decompose carbonic acid and fix the carbon necessary to their sustenance. A knowledge of these circumstances lies at the basis of many horticultural operations. Celery and endive are rendered delicate by studiously protecting them from the light. For the same reason, the interior of a cabbage is white. Not only is there a difference in the colour of vegetables thus circumstanced; there are also differences of chemical composition. The secretions are all modified. Thus, wild celery is rank and somewhat poisonous, garden celery is innocuous, wild sea-kale is so disagreeable to the taste that it could not be eaten without disgust—cultivated sea-kale is tender, and almost insipid.

Although the general influence of solar rays on vegetable life is so well known, the immediate mode of agency of the power—"actinism," "tithonicity," "energia," or whatever we may call it—is still unknown.

Mr. Robert Hunt, who has devoted so much of his attention to the study of non-calorific non-luminous radiant matter, has arrived at some curious deductions relative to the influence of solar rays on vegetables. He finds that yellow light is more unfavourable than any other to vegetation—blue or violet the most favourable. Now it has been already shown that these colours correspond with the maximum and minimum chemical effect in heliographic processes.

Passing from the natural chemical operations of horticulture and agriculture to those of the laboratory, abundant instances can there be shown of the influence of chemically-acting radiant matter. Chlorine and hydrogen gases may be retained mixed in the dark for an almost indefinite period; exposed to diffuse light, a slow combination takes place,—but if exposed to the broad glare of sunlight, then combination ensues with such readiness that an explosion is the result. Moreover, it is a curious fact, that if chlorine be exposed to the action of the sunbeam, and afterwards mixed with hydrogen, it will have acquired the power of combining with the latter.

Chlorine and carbonic acid furnish another parallel instance. If allowed to remain in contact in the dark, these gases will not unite; but mixed and exposed to sunlight, combination ensues, and phosgen gas, as it is called, with reference to the cause of its generation, results. Sir Robert Kane has mentioned, in addition to the above, two very curious instances of chemical action promoted by solar beams. In the dark, or a moderately darkened room, chlorine exerts scarcely any action on pyroxylic spirit; whereas, in sunshine, combination ensues with explosive violence. But the second, and still more curious exemplification mentioned by Sir Robert Kane, is the following:—

When that gentleman was in Paris, operating in concert with Professor Dumas, he succeeded in removing, by means of chlorine, two equivalents of hydrogen from acetone, changing it from the original composition, indicated by the formula $C_3 H_3 O$, to a chlorine compound indicated by $C_3 H Cl_2 O$. On no occasion, however—even during the height of summer, when operating at Dublin—could he succeed, by a similar treatment, in removing more than one equivalent of hydrogen, and generating the compound indicated by $C_3 H_2 Cl O$.

The foregoing examples will serve to impress the student with the importance of that connexion, yet but ill understood, subsisting between chemical action and that peculiar associate of light which has been termed by different chemists actinism, tithonism, and energia.

Luminous Epipolic Dispersion.—The term epipolic dispersion was first applied by Sir John Herschel to indicate a series of phenomena which have also been studied by Sir David Brewster, but still more carefully by Professor Stokes of Cambridge. This latter philosopher has arrived at some very important conclusions relative to the class of phenomena in question; the most striking of which being, that the prismatic spectrum is not composed of the three different agents, heat, light, and actinism, but probably two, light and actinism being different functions of the same; and it may be that even the heating part of the spectrum is only a third variety of manifestation of one and the same agent.

In anticipation of the experiments by which Professor Stokes arrives at his conclusions, it may be here stated that he imagines his investigations warrant the conclusion that the refrangibility of light for each colour is not fixed and invariable as, since the time of Newton, has been universally imagined, but that light of one colour admits of being changed, under certain circumstances, into light of another colour; and, more curiously still, that the actinic or non-luminous part of the prismatic spectrum admits, under certain circumstances, of being rendered visible.

The phenomenon to which the attention of Sir J. Herschel was first directed in relation to epipolic dispersion of light is one that most persons will have noticed. If a weak solution of pharmaceutical disulphate of quinine in water, slightly acidulated with sulphuric acid, be regarded under certain conditions of daylight, a peculiar blue opalescence will be observed to pervade its surface, and to extend a short way down into its bulk; but if the light, which has once been transmitted through a solution of sulphate of quinine, be made to impinge on another solution precisely similar in all respects, the original phenomenon will not be repeated,—thus leading to the inference that (to use a popular expression) some peculiar quality of the light has been removed, or strained away.

In one experiment performed by Sir J. Herschel, in which sunlight was used, a pale blue flame extended to nearly half an inch from the surface. As regards the dispersed light, this, when analyzed by a prism, was found to consist of rays extending over a great range of refrangibility; the less refrangible extremity, however, of the spectrum was wanting. The dispersed light, on being analyzed by a tourmaline, showed no signs of polarization. Another experiment showed that the dispersed light was perhaps incapable, at any rate not peculiarly susceptible, of being again dispersed.

Such is the nature of the phenomenon as evidenced by a solution of disulphate of quinine; numerous other bodies, however, both solid and liquid, manifest a similar property. Some time before the attention of Sir John Herschel had been drawn to the peculiar phenomena of blue epipolic dispersion in a quiniferous solution, Sir David Brewster had noticed a peculiar exhibition of red light by certain green vegetable solutions—the green matter of leaves, for example. In this case the colour is not limited to a thin stratum of the surface, as is the case with a quiniferous liquid; but Professor Stokes, nevertheless, considers it to be a phenomenon of the same kind. In both cases the curious point for contemplation was this:—A ray of light by passing across a stratum of liquid was deprived of the power to reproduce the original effect; still, in no other respect did it appear to be altered. "I found myself, therefore," remarks Professor Stokes, "fairly driven to suppose that the change of nature consisted in a change of refrangibility. From the time of Newton it had been believed that light retains its refrangibility through all the modifications which it may undergo

Nevertheless, it seemed to me less improbable that the refrangibility of light should have changed, than the undulatory theory should have remained at fault. We have only to suppose that the invisible rays beyond the extreme violet give rise, by internal dispersion, to others which fall within the limits of refrangibility, between which the retina of the human eye is affected, and the explanation is obvious. The narrowness of the blue band observed by Sir John Herschel would merely indicate that the fluid, though highly transparent with regard to the visible rays, was nearly opaque with regard to the invisible ones. According to the law of continuity, the passage from almost perfect transparency to a high state of opacity would not take place abruptly. We should thus, too, have an immediate explanation of a remarkable circumstance connected with the blue band—namely, that it can hardly be seen in strong candle-light, though readily seen by even weak daylight; for candle-light, as is well known, is deficient in the chemical rays situated beyond the extreme violet."

Although a solution of disulphate of quinine is the body in which the phenomena of internal luminous dispersion were first studied, it is by no means the only one; nor is it even that in which the phenomenon in question is most strikingly developed. The following list comprehends the substances in which the quality of internal luminous dispersion is most observable:—

LIST OF HIGHLY SENSITIVE SUBSTANCES.

Glass, coloured by peroxide of uranium, yellow uranite, nitrate or acetate of the peroxide. Probably various other salts of the peroxide would do as well. The absorption bands of the salts, whether sensitive or not, of peroxide of uranium, ought to be studied in connexion with the change of refrangibility.

A solution of the green colouring matter of leaves in alcohol. To obtain a solution which will keep, it is well previously to steep the leaves in boiling water. The alcohol should not be left permanently in contact with the leaves, unless it be wished to observe the changes which, in that case, take place; but poured off when the strength of the solution is thought sufficient. Also the solution, when out of usé, must be kept in the dark.

A weak solution of the bark of the horse-chestnut.

A weak solution of sulphate of quinine—*i. e.*, a solution of the common disulphate, in very weak sulphuric acid. Various other salts of quinine are nearly, if not quite, as good.

Fluor spar (a certain green variety).

Red sea-weeds, of various shades; a solution of the red colouring matter in cold water. If a solution be desired, a sea-weed must be used which has never been dried.

A solution of the seeds of *Datura stramonium* in alcohol, not too strong.

Various solutions obtained from archil and litmus.

A decoction of madder in a solution of alum.

Paper washed with a pretty strong solution of sulphate of quinine, or with a solution of stramonium seeds, or with tincture of turmeric. The sensibility of the last paper is increased by washing it with a solution of tartaric acid. This paper ought to be kept in the dark.

A solution, not too strong, of guiacum in alcohol.

Safflower-red, scarlet cloth, substances dyed red with madder, and various other dyed articles in common use.

Many of the solutions here mentioned are mixtures of various compounds. Of course if the sensitive substance can be obtained chemically pure it will be all the better.

The following are the chief deductions which have been arrived at from a consideration of Professor Stoke's experiments:—

1. In the phenomena of true internal dispersion, the refrangibility of light is changed, incident light of definite refrangibility giving rise to dispersed light of various refrangibilities.

2. The refrangibility of the incident light is a superior limit to the refrangibility of the component parts of the dispersed light.

3. The colour of light is in general changed by internal dispersion, the new colour always changing to the new refrangibility. It is a matter of perfect indifference whether the incident rays belong to the visible or invisible part of the spectrum.

4. The nature and intensity of the light dispersed by a solution appears to be strictly independent of the state of polarization of the incident rays. Moreover, whether the incident rays be polarized or unpolarized, the dispersed light offers no traces of polarization. It seems to emanate equally in all directions, as if the fluid were self-luminous.

5. The phenomenon of a change of refrangibility proves to be extremely common, especially in the case of organic substances, such as those ordinarily met with, in which it is almost always manifested to a greater or less degree.

6. It affords peculiar facilities for the study of the invisible rays of the spectrum more refrangible than the violet, and of the absorbing action of media with respect to them.

7. It furnishes a new chemical test of remarkably searching character, which seems likely to prove of great value in the separation of organic compounds. The test is specially remarkable for this, that it leads to the independent recognition of one or more sensitive substances in a mixture of various compounds, and shows to a great extent, before such substances have been isolated, in what menstrua they are soluble, and with what agents they enter into combination. Unfortunately, these observations, for the most part, require sunlight.

8. The phenomena of internal dispersion oppose fresh difficulties to the supposition of a difference of nature in luminous, chemical, and phosphorogenic rays, but are perfectly conformable to the supposition that the production of light, of chemical changes, and of phosphoric excitement, are merely different effects of the same cause. The phosphorogenic rays of an electric spark, which, as is already known, are intercepted by glass, appear to be nothing more than invisible rays of excessively high refrangibility, which there is no reason for supposing to be of a different nature from the rays of light.

The reader who desires further information relative to this novel and curious subject will find it treated at greater length, and in a more practical manner, in the volume of APPLIED CHEMISTRY, which will succeed this volume.

OF HEAT OR CALORIC.

General Observations on Heat.—When we apply the hand to a body which is hotter than itself, we are sensible of a peculiar feeling, which we agree to call the sensation of heat. At the same time we observe, in almost all bodies that are placed in the same situation with the hand, certain effects, the most remarkable of which is an enlargement of their dimensions. These circumstances, with very few exceptions, so constantly accompany each other, that we can have no hesitation in referring them to one and the same cause. Of the nature of this cause we have no satisfactory evidence; and we are unable to demonstrate either that it consists in any general quality of bodies, or that it resides in a distinct and peculiar kind of matter. The opinion, however, which best explains the phenomena is that which ascribes them to an extremely subtile fluid, of so refined a nature as to possess no sensible weight, and to be capable of insinuating itself between the particles of the most dense and solid bodies. To this fluid, as well as the sensation which it excites, the term heat was formerly applied. But there was thought to be an obvious impropriety in confounding under one appellation two things so distinct as a sensation and its cause; and the term *caloric*, first proposed by Lavoisier, is now frequently adopted to denote the *cause of heat*. Occasionally, however, in order to avoid too frequent repetition of the same word, the term heat is still employed in a more extensive sense, to express not only the sensation which it usually denotes, but also some of the modifications of caloric; and as the context generally shows in which sense the term is to be understood, I shall not scruple to use it in both.

Caloric, so far as its chemical agencies are concerned, may be chiefly considered under two views—as an antagonist to the cohesive attraction of bodies, and as concurring with and increasing elasticity. By removing the particles of any solid to a greater distance from each other, their cohesive attraction is diminished; and one of the principal impediments to their union with other bodies is overcome. On the other hand, caloric may be infused into bodies in such quantity as not only to overcome cohesion, but to place their particles beyond the sphere of mutual attraction. Thus, in the class of substances called gases, the *base* or ponderable ingredient, whether solid or liquid, is dissolved in so much caloric, that, with few exceptions, the bases of different gaseous bodies do not unite by simple mixture of the gases themselves. But if of two gases we employ either one or both in a state of great condensation, the gravitating matter of both unites, and forms a new compound. Hydrogen and nitrogen gases, for example, may be mingled together, in the proportions adapted to form ammonia, without any production of that compound. But if hydrogen, in what has been called its *nascent state* (that is, before it has acquired an atmosphere of heat, and become gaseous), be brought into contact with nitrogen gas, ammonia is then generated. In many cases, also, when two bodies are combined together, one of which is fixed, and the other becomes elastic by union with caloric, we are able, by its interposition alone, to effect their disunion. Thus carbonate of lime gives up its carbonic acid by the mere application of heat.

We may consider, then, all bodies in nature as subject to the action of two opposite forces—the mutual attraction of their particles on the one hand, and the repulsive power of caloric on the other; and bodies exist in the solid, liquid, or elastic state, as one or the other of these forces prevails. Water, by losing caloric, has its cohesion so much

increased, that it assumes the solid form of ice; adding caloric, we diminish its cohesion, and again render it fluid; and finally, by a still further addition of caloric, we change it into vapour, and give it so much elasticity, that it may be rendered capable of bursting the strongest vessels. In many liquids, the tendency to elasticity is even so great, that they pass, at common temperatures, to the gaseous form, by the mere removal of the weight of the atmosphere.

Caloric, like all other bodies, may exist in two different states—in a state of freedom, and in a state either of combination or of something nearly resembling it. In the former state it is capable of exciting the sensation of heat, and of producing expansion in other bodies. To this modification the terms *free* or *uncombined caloric*, or *caloric of temperature*, have been applied. By the term *temperature*, we are to understand the state of a body relatively to its power of exciting the sensation of heat, and occasioning expansion; effects which, in all probability, bear a proportion to the quantity of free caloric in a given space, or in a given quantity of matter. Thus, what we call a high temperature may be ascribed to the presence of a large quantity of free caloric; and a low temperature to that of a small quantity. We are unacquainted, however, with the extremes of temperature; and may compare it to a chain, of which a few of the middle links only are exposed to our observation, while its extremities are far removed from our view.

The degree of expansion produced by caloric, it will afterwards appear, bears a sufficient proportion to its quantity to afford us a means of ascertaining the latter with tolerable, though not perfect accuracy. In estimating temperature, indeed, our senses are extremely imperfect; for we compare our sensations of heat, not with any fixed or uniform standard, but with those sensations of which we have had immediately previous experience. The same portion of water will feel warm to one hand removed from contact with snow, and cold to the other hand which has been heated before the fire. To convey, therefore, any precise notion of temperature, we are obliged to describe the degree of expansion produced in some one body, which has been previously agreed upon as a standard of comparison. The standard most commonly employed is a quantity of quicksilver, contained in a glass ball, which terminates in a long narrow tube. This instrument, called a *thermometer*, is of the most important use in acquiring and recording our knowledge of the properties and laws of caloric. The thermometer, however, it must be obvious, is no otherwise a measurer of the quantity of caloric than as it ascertains the amount of one of its principal effects. In this respect, it stands in much the same predicament as the hygrometers of Saussure or Deluc, when considered as means of determining the moisture of the atmosphere. These last instruments, it may be remembered, are composed of some substance (such as a human hair or a slip of whalebone) which is lengthened by a moist atmosphere, and contracted by a dry one; and in a degree proportionate to the moisture or dryness. But all the information which hygrometers of this sort give us is the degree of moisture between certain points that form the extremities of their scales; and they are quite incompetent to measure the absolute quantity of watery vapour in the air.

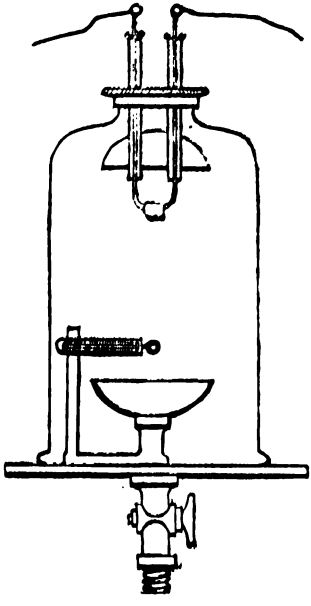
In explaining those properties and laws of caloric which have become known to us by means of the thermometer, it appears a sufficiently natural division of the subject to describe, firstly, those effects which caloric produces, without losing its properties of exciting the sensation of heat and occasioning expansion; and, secondly, those agencies in which its characteristic properties are destroyed, and in which it ceases to be cognizable by our senses or by the thermometer.

The *expansion* or *dilatation* of bodies, it will appear, is an almost universal effect of an increase of temperature. Its amount, however, is not the same in all bodies, but differs very essentially. By the same increase of temperature, liquids expand more than solids, and aëriform bodies much more than either. Nor is the same quantity of expansion effected in the *same* solid or liquid, at all temperatures, by adding similar quantities of heat; for, generally speaking, bodies expand by equal increments of caloric, more in high than in low temperatures. The explanation of this fact is, that the force opposing expansion (*vis.* cohesion) is diminished by the interposition of caloric between the particles of bodies; and, therefore, when equal quantities of caloric are added in succession, the last portions meet with less resistance to their expansive force than the first. In gases, which are destitute of cohesion, equal increments of heat appear, on the contrary, to be attended with nearly equal augmentations of bulk.

An important property of free caloric, the knowledge of which has been acquired by means of the thermometer, is its *tendency to an equilibrium.* Twenty or thirty different bodies, for instance, all unequally heated, soon arrive, when exposed in a still atmosphere, at an equality of temperature. When a heated ball of iron is exposed to the open air, the caloric, which is accumulated in it, flows out; and the temperature of the ball is gradually reduced to that of the surrounding medium. This is owing to two distinct causes: the air immediately surrounding the ball acquires part of the caloric which escapes; and, having its bulk increased, is rendered specifically lighter, and ascends. This is succeeded by a cooler and heavier portion of air from above, which in its turn is expanded, and carries off a second quantity of caloric. Hence a considerable part of the caloric, which is lost by a heated body, is conveyed away by the ambient air—a property of which advantage is taken in the warming and ventilating of apartments. But the refrigeration cannot be wholly explained on this principle; for it has been long known that heated bodies cool, though with less celerity, under the exhausted receiver of an air-pump, and even in a Torricellian vacuum.

When the phenomena accompanying the cooling of bodies are accurately examined, it is found that a part of the caloric which escapes moves through the atmosphere with immeasurable velocity. In an experiment of M. Pictet, no perceptible interval took place between the time at which caloric quitted a heated body, and its reception by a thermometer at the distance of sixty-nine feet. It appears also, from the experiments of the same philosopher, to move with equal ease in all directions, and not to be at all diverted from its course by a strong current of air meeting it transversely. Hence it follows that the propagation of caloric, in this state of rapid movement, does not depend on any agency of the medium through which it passes. This was satisfactorily proved by Sir H. Davy, who contrived, by means of the apparatus represented on the following page, to effect the radiation of heat *in vacuo.* Between the points of two wires, inclosed in glass tubes, which passed through a brass plate, was placed a piece of charcoal, which was intensely ignited by voltaic electricity, and the effect of radiation in the focus of the lower concave mirror was ascertained by a delicate thermometer, first when the receiver was full of air, and next when it was exhausted to $\frac{1}{120}$. In the latter case, the effect of radiation was found to be three times greater than in an atmosphere of common density. The greater rise of the thermometer in vacuo than in air is to be ascribed to the conducting power of the latter; for this conducting power, by reducing the temperature of the heated body, has a constant tendency to diminish the activity of radiation, which is always proportional to the excess of temperature of the heated body above that of the surrounding medium.

Heat is invisible, and devoid of weight. The latter proposition may be demonstrated by weighing a portion of oil of vitriol and another of water, mixing the two, when great heat will be developed. Allowing the mixture to cool, and finally weighing it when cold, the weight will not be altered. It is elastic and repulsive; hence two heated bodies, placed under the vacuum of an air-pump, and admitting of free motion, repel each other.*



Another and more elegant means of demonstrating the same fact was pointed out by Professor Baden Powell. It is as follows:—If a lens be laid with its convexity on a glass plate,

and the eye directed vertically upon it, coloured rings will be seen dependent, as was shown in the chapter on light, upon the varying approximation of the lenticular convexity to the glass plane. If the combination be heated, the colours of the rings will change, proving that repulsion has taken place.

Like light, heat appears to be transmitted in parallel rays; and when thus in motion, it has been called *radiant caloric*. The comparative quantities of caloric lost by radiation and by conduction may be approximated by observing what time a body takes to cool, through the same number of degrees, in air and in vacuo. By experiments of this kind, Dr. Franklin thought he had ascertained that a body, which requires five minutes in vacuo, will cool in air, through the same number of degrees, in two minutes. Count Rumford's experiments with a Torricellian vacuum give the proportions of five in vacuo to three in air. It will, perhaps, not be very remote from the truth, if it be stated, in general terms, that one half of the caloric lost by a heated body escapes by radiation, and that the rest is carried off by the ambient atmosphere.

The rate of cooling in air appears to bear a proportion to the elevation of temperature of a body above that of the surrounding medium. Hence, in part, it is that a heated body, during refrigeration, loses unequal quantities of caloric in equal times. The series makes some approach to a geometrical one. Thus, supposing the temperature of a body to be 1000 degrees above the surrounding medium—

In the first minute it will lose $\frac{9}{10}$ of its heat, or . . 900°
In the second . . . . . $\frac{9}{10}$ of the remainder = 90°
In the third . . . . . $\frac{9}{10}$ of 10 . . . . = 9°.

This law of refrigeration, originally laid down by Newton, though nearly accurate at low temperatures—*i. e.* between 68° and 86° Fah.—it has been shown by Delaroche,

* Fresnel, "Ann. Chem. Phys.," 30, 37, and 107.

is far from being so at high ones; and his objections have been fully confirmed by Petit and Dulong, who have proved that the error increases as the temperature augments, and at length becomes enormously great.*

According to M. Quetelet, the following is an abstract of the researches of MM. Dulong and Petit in this important investigation:—

When a body cools, it is necessary to take cognisance of the loss occasioned by radiation as well as that referable to contact with the air.

If it were possible to observe the rate of cooling of a heated body placed in a vacuum, bounded by a limit absolutely devoid of heat, and deprived of the faculty of radiating, the velocity of cooling would decrease in geometric ratio, whilst the temperatures would diminish in arithmetic ratio. The temperature of the vacuum containing the heated body being supposed to remain constant, the rapidity of cooling of the latter, as regards its excess of heat over that of the vacuum, would decrease, as the terms of a geometric proportion diminished, by a constant number. The ratio of this geometric progression is the same for all bodies, being equal to 1·0077.

The rapidity of cooling in vacuo for the same excess of temperature increases in geometric proportion, the temperature of the inclosed space increasing in arithmetic proportion. Hence the relation of the progression still remains 1·0077 for all bodies. The rapidity of cooling referable to the simple contact of a gas is altogether independent of the nature of the surface of such bodies. The rapidity of cooling due to the simple contact of a fluid varies in geometric progression, whilst the excesses of temperature themselves vary in geometric proportion. If the ratio of this second progression be 2, the ratio of the first is 2·35, whatever may be the nature of the gas, and the degree of its elastic force. This law may also be enunciated by saying that the quantity of heat removed by a gas is in all cases proportional to the excess of temperature of the body elevated to the power of 1·233. The cooling power of a fluid diminishes in geometric progression, when its tension also diminishes in the same progression. If the ratio of this second progression be 2, the ratio of the former is 1·366 for air, 1·301 for hydrogen, 1·431 for carbonic acid, and 1·415 for olefiant gas.

The law may be presented also under a third aspect, as follows:—The cooling power of a gas is, *ceteris paribus*, proportional to a certain force of pressure. The exponent of this power, which depends on the nature of the gas, is 0·45 for air, 0·315 for hydrogen, 0·517 for carbonic acid, and 0·501 for olefiant gas. The cooling power of a gas varies with its temperature in such manner that, provided such gas be dilatable, and that it preserve its elastic force, the cooling power will be diminished by rarefaction of the gas, in direct commensurate proportion with the amount of its augmentation by heating, in such a manner that the tension of the gas alone remains to be estimated.

The movement of caloric by radiation occurs only in free space, or through transparent media. It appears to be the same through all the different varieties of aëriform bodies; though, as will afterwards appear, the gases differ materially from each other in their *conducting power*. Caloric radiates from bodies at all temperatures, but the quantity radiated in a given time bears some proportion to the excess of the temperature of the hot body above that of the surrounding medium. So also does its *intensity* or *tension*, for the higher the temperature of its source, the more readily, *ceteris paribus*, does radiated caloric penetrate glass and other diathermanous† transparent bodies. And if we have any number of bodies at different temperatures in the vicinity of each other,

* "Annals of Philosophy," vol. xiii. † This term will be presently explained.

they may all, agreeably to the ingenious theory of M. Prevost, be considered both as radiating and receiving caloric; but the hot ones will radiate more than they receive, while the cold ones will receive more than they radiate.

The process of radiation appears to be constantly going on from the surface of the earth, and it is partly on this principle that we are to explain why the heat, which our planet is incessantly receiving from the sun, does not accumulate to such a degree as to render it a less fit habitation for man. The period when radiation from the surface of the globe is most discoverable by its effects, seems to be during the night, especially when the sky is perfectly unclouded; for a covering of clouds serves as a mantle to the earth, which not only prevents the free escape of radiant heat, but probably radiates it back to the earth's surface. Under favourable circumstances, it has been shown by Dr. Wells, that the temperature of the ground, especially when its covering is formed of some substance that radiates freely, is several degrees below that of the atmospheric stratum, a few feet above it. It is this diminished temperature of the earth's surface that occasions the deposition of dew and hoar frost, which are always observed to be most abundantly formed under a clear unclouded sky.

Radiant Heat.—*Relative facility with which transparent bodies admit the passage of radiant heat.*—The difficulty with which radiant heat evolved from certain sources traverses glass and other transparent materials, was noticed at a very early period; and the generalization, very incorrect as will be seen, was arrived at, that radiant heat from no terrestrial source could permeate glass or other transparent body. This opinion was demonstrated by Professor Brande, in the year 1820, to be erroneous, for one source of terrestrial radiant heat at least; namely, that developed from charcoal points under the influence of voltaic electricity.*

Professor Daniell subsequently demonstrated a similar result for incandescent lime.†

But an experiment is scarcely needed to show the fallacy of the assumption. Any one who stands outside a glass window whilst a gas jet is suddenly lighted inside, must be sensible of the passage of heat.

The generalization that no transparent body would admit the passage of terrestrial radiant heat being found untenable, a question arose as to the nature assumed by the heat during its passage through the transparent body. On the one hand, it was argued that the heat traversed the intercepted layer by radiation, as it traverses air and other gases: on the other hand, it was argued that on coming into contact with one side of the intercepted layer, the radiant heat was absorbed, and passed by conduction to the other side of the layer, whence it was finally radiated away. M. Prevost settled this controversy by a very ingenious experiment. He used, as his interposed transparent screen, a sheet of water issuing from a fountain; still heat was recognised on the farther side, which result could only be attributable to the passage of heat by radiation. Not only is water a bad conductor of heat, but the conduction, if it had taken place, would have been in the direction of the water from the fountain, not at right angles to it.

No precise generalization of the laws affecting the passage of radiant heat through transparent bodies was, however, arrived at, until the adoption of an instrument more delicate than the thermometer as an indicator of temperature. This instrument was found in the *thermomultiplier* of Nobili—an instrument dependent on electricity

* "Phil. Trans.," 1820. † "Phil. Mag.," New Series, p. 391.

as its prime motive agent, and which, under the head of Electricity, will be fully described.

In the hands of Signor Melloni,* Professors Forbes, Powell, and other philosophers, this instrument has demonstrated the remarkable fact, that the transparency of a substance has no necessary relation to its function of transmitting radiant heat. Hence arises the necessity for terms corresponding with transparency and opacity, as applied to light. The expression, *transcalency*, has been applied to indicate the function of allowing the passage of radiant heat, and *non-transcalency* the reverse. Hence, we have transcalent and non-transcalent substances,—otherwise called diathermanous and a-diathermanous, and corresponding with the expressions *diaphanous* and *a-diaphanous*.

Melloni's experiments demonstrated furthermore that the ability of radiant heat to pass through transcalent sheets, varied according to the source from which the heat emanated—and that, of all substances tried, only rock-salt was endowed with the power of transmitting a constant amount of heat—from whatever source derived. Hence, rock-salt is the most diathermanous or transcalent body known, and may be considered, in relation to heat, as perfectly white transparent glass is to light. On the other hand, the transparent substance which, of all others, opposes the greatest resistance to the passage of radiant heat, is sulphate of copper. Rock-salt transmits, according to Melloni, 92 per cent. of radiant heat impinging upon it, from whatever source derived; whilst, on the other hand, a plate of sulphate of copper, equal or even less as to thickness, transmits none: it is the precise analogue of opacity. It has been also demonstrated by Melloni, that radiant heat from any given source, having suffered diminution by passing through a transcalent medium, should be capable of passing through other similar media with less proportionate loss than it experienced on passing through the first. Thus, the heat which has already traversed one plate of glass, becomes less susceptible of absorption on passing through others; and on establishing the proportion of loss in a thousand parts, it was found that of 1000 rays of heat from the flame of an oil lamp, 451 were intercepted by four plates of glass of equal thickness. Of these rays, 381 were intercepted by the first plate, 43 by the second plate, 18 by the third, and the remaining 9 by the fourth. This result leads to the supposition that just as there are different colours of light, so, if the term be permitted, are there different colours of heat; that radiant heat consists of a mixture of these colours, from which one or more having been abstracted by one particular medium, the transmitted heat radiates through other media of similar kind without subsequent loss.

It has been pertinently remarked by Professor Baden Powell,† that the per centage indication of light transmitted through screens, as employed by Melloni, creates the assumption that the heat is of one kind; whereas the results are only accordant with the assumption that it is of many kinds. Professor Powell also objects to the division of radiant heat into that from luminous and non-luminous sources. No precise distinction of this kind, it is argued, can be laid down; for although certain qualities (colours, so to say) of heat may predominate in either case, yet the only resulting variation is one of excess or diminution of one set of ray or rays.

It is an opinion also of the above-mentioned philosopher, that the phenomena con-

* *Vide* Melloni's papers in the "Ann. de Chim." and "Ph." LIII. and LV., also "Taylor's Scientific Memoirs," I. and III.

† Royal Institution Reports. Report of Professor B. Powell's lecture, Friday, April 23, 1852.

nected with this interesting subject point to the identity of cause for light and heat. Thus both depend on corpuscular vibrations, and are explicable by an extension of the luminous undulatory theory, which has been treated of in the chapter on light. Professor B. Powell is inclined to refer the different qualities (colours) of radiant heat, to a difference in the length of wave line exclusively. Professor Forbes, whilst partially agreeing in this view, suggests the coexisting agency of some undetermined element. Professor Melloni does not accede thus far: he is in favour of the existence of calorific emanations altogether different, even as to their original cause, from those of light.

It would be incompatible with the limits and the intentions of this treatise to follow out the subject of diathermaniety and its converse in detail. I will, therefore, conclude by citing the concluding generalization of Professor Baden Powell, as expressed in his paper, read before the members of the Royal Institution.

"A body heated below luminosity begins to give out rays of large wave-length only. As it increases in luminosity it continues to send out these, and at the same time others of diminishing wave-lengths, till at the highest stage of luminosity it gives out rays of all wave-lengths, from those of the limit, greater than the red end of the spectrum, to those of the violet end, and possibly less.

"Rays of all these species are transmissible and refrangible by rock-salt; and many of them, with numerous specific distinctions, by other media. They are all more or less capable of exciting heat when absorbed or stopped; though in some the effect is perhaps insensible. Both this property and that of their transmissibility seems to depend, in some way, on the wave-lengths, although in no simple ratio to it.

"The absorptive effect due to texture of surface has some direct relation to the magnitude of the wave-length, especially near the limit; while that due to darkness of colour is connected with shorter wave-lengths—such as belong to rays within the limits of the light spectrum; and in any case when a ray impinges on any absorbing substance, its vibrations being stopped, communicate to the molecules of the body vibratory movements of such a kind as constitute heat of temperature.

"The peculiar molecular constitution of bodies, which determines their permeability or impermeability to rays of any species, gives rise to all the diversities of effect, whether luminous or calorific. We thus escape all such crude ideas, at once difficult and unphilosophical, as those either of two distinct material emanations producing respectively heat and light, or of a conversion of one into the other; and obtain a view far more simple and consistent with all analogy."*

Polarization and Double Refraction of Radiant Heat.—The many analogies subsisting between light and radiant heat, created an *à priori* opinion that the latter might be polarized. Bérard and Professor Forbes† first demonstrated the correctness of this idea. They succeeded in polarizing heat (non-luminous) by the agency of reflection. Subsequently Melloni effected a similar polarization by transmission through mica and tourmaline respectively. I deem it unnecessary to treat

* For the convenience of those who desire to study this interesting subject more deeply, the following additional references to books and papers relating to it is appended :—

Vide 1. "Two Reports on the State of our Knowledge of Radiant Heat," by Professor Baden Powell. "Brit. Assoc. Reports," 1832 and 1840. (These papers supply copious references.)

2. A paper by the same in "Phil. Trans." for 1823.

3. "Knoblauch's Researches," translated in "Taylor's Scientific Memoirs," Parts XVIII. and XIX.

4. Powell on the "Undulatory Theory Applied to the Dispersion of Light," pp. 71—122.

† "Phil. Mag.," 1835.

more in detail on this subject, seeing that the phenomena of polarized heat are so precisely accordant with those of polarized light, already treated of in detail in the chapter on light.

Caloric, besides radiating through transparent media, is capable, also, of passing through dense and opaque bodies, though with prodigiously impaired velocity. Thus a long bar of iron, heated at one end, requires considerable time to become hot at the other. This property in bodies has been called their conducting power, and it exists, in different bodies, in very different degrees. It is not, however, found to bear a proportion to any other quality of bodies, such as their densities, &c.

All the properties of caloric, which have been hitherto described, belong to it when supposed to be in a free or uncombined form; for it continues to produce the sensation of heat, and to expand the mercury of the thermometer. In the instances of its agency, also, that have been mentioned, no permanent change of form or of properties is effected in the bodies which have imbibed caloric. A bar of iron, after being expanded by heat, returns on cooling to the same state as before, and exhibits all its former qualities. In certain cases, however, caloric is absorbed by bodies, with the loss of its distinguishing properties. It can then be no longer discovered by our senses or by the thermometer; and it produces important and sometimes permanent changes in the bodies into which it enters.

Those effects of caloric, in the production of which it loses its distinguishing properties, may be classed under two general heads.

1. *Bodies, in passing from a denser to a rarer state, generally absorb caloric.*—Thus solids, during liquefaction, imbibe a quantity of caloric, which ceases to be apparent to our senses or to the thermometer; or, as it has been termed, *becomes latent.* In a similar manner, solids and liquids, during their conversion into vapours or gases, render latent a quantity of caloric, which is essential to the elasticity of the new product. In common language cold is, in such cases, said to be produced; but by the production of cold we are to understand, in philosophical language, nothing more than the passage of caloric from a free to a latent form.

2. *Bodies, by an increase of density, mostly evolve or give out caloric, which passes from a latent to a free state.*—The simplest illustration of this law is in the effect of hammering a piece of metal, which may thus be intensely heated, while all that is permanently effected is an augmentation of its density. Liquids by becoming solids, or gases by conversion into liquids, also evolve caloric, or produce an increase of temperature. A pound of water condensed from steam, will render 100 pounds of water at 50° warmer by 11°; whereas a pound of boiling water will produce the same rise of temperature in no more than about 15⅓ pounds. This is owing to the much greater quantity of caloric, existing in a pound of steam, than in a pound of boiling water, though steam and boiling water affect the thermometer in precisely the same degree.

It is a question which has excited considerable interest among philosophers, whether caloric, when thus absorbed and rendered latent, enters into chemical combination, or is merely united by the same kind of ties as that portion of caloric that produces the temperature of bodies. Does ice, for example, when changed into water, form a chemical union with caloric, similar to that which exists between potassa and sulphuric acid? Such appears to have been the opinion of Dr. Black, who, by the powers of an original and well-directed genius, discovered, about the year 1760, the greater number of those facts, that formed the ground-work of the theory of latent heat. The resemblance, however, between chemical union and the disappearance of caloric, which, on

first view, appears extremely striking, will be found, it must be confessed, less close on a nearer examination; for caloric may be made to quit those bodies, into which it has entered with a loss of its peculiar properties, merely by reducing their temperature; whereas chemical combinations in general cannot be destroyed, except by the interference of more energetic affinities. In opposition to the foregoing theory, it has been contended that the absorption of caloric by bodies is a consequence of what has been called a change of their *capacity*. Thus ice, it is supposed, in becoming water, has its capacity for caloric increased, and the absorption of caloric is regarded as a consequence of this increased capacity. This theory, however, is deficient, inasmuch as it fails to explain what is the cause of that change of form, which is assumed to account for the increase of capacity. Notwithstanding this obvious objection, I have retained the term *capacity* to express, in the abstract, that power by which bodies absorb and render latent different quantities of caloric; or the property of requiring more or less caloric for raising their temperature an equal number of degrees. The absorption of caloric, then, will always be owing to an increase, and its evolution to a decrease, of capacity. The use of these terms may be exemplified by a slight change of the perspicuous language of Dr. Crawford. "The capacity for containing caloric," he observes, "and the absolute caloric contained, are distinguished as a force from the subject upon which it operates. When we speak of the *capacity*, we mean a power inherent in the heated body; when we speak of the *absolute caloric*, we mean an unknown principle, which is retained in the body by the possession of this power; and when we speak of the *temperature*, we consider the unknown principle as producing certain effects upon the thermometer."*

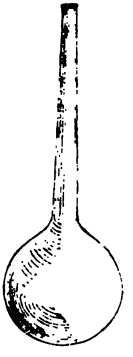
As the capacities of bodies determine their relative quantities of caloric, it seems reasonable to conclude that, if we can ascertain how much caloric a body absorbs or gives out in changing its form, and in what proportion its capacity is at the same time altered, we may deduce the *absolute quantity of heat* which it contains. Now it will be afterwards shown that the heat, evolved by water in freezing, is equal to 140°; and the capacity of water has been stated to bear to that of ice the proportion of 10 to 9. Water, then, in becoming ice, must give out $\frac{1}{10}$th of its whole caloric; and, as this amounts to 140°, ten times 140 (or 1400°) is the whole quantity of caloric in water at the temperature of 32°; and, deducting 140 from 1400, we have 1260° for the caloric contained in the ice itself. This method of determining the problem seems, however, to me, to be liable to several objections, which it would take up too much room to state in this place, and which I have elsewhere urged at considerable length.† Nor does it appear to me that any other mode of investigation yet proposed is capable of giving us approximations to the truth, that are more to be relied on; for such enormous differences as to the absolute zero, or point of total privation of heat on the thermometric scale, have resulted from the inquiries of different philosophers, as to show that we still want the data essential to such an investigation.

These general observations I have deemed it necessary to make, with a view of connecting together the propositions respecting caloric, and the experiments illustrating them, that form the subject of the following sections. The inquiry respecting heat is one which presents a boundless field for interesting speculation; and it would have been easy to have extended very considerably the discussion of its nature and properties. But, in this work, I have no further object than to lead the student, by

* See Crawford on Heat, p. 5. † "Manchester Memoirs," vol. v.

steps, to a knowledge of what has been actually determined by experiment, or tly and legitimately deduced from it.

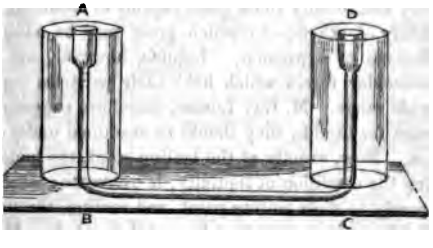
The Effects of Free Caloric.—1. *Caloric expands all bodies.*—The expansion of *ds* is shown by that of the mercury of a thermometer, or by immersing in hot water ss matrass, filled, up to a mark in the neck, with spirit of wine, tinged with any uring substance. The spirit expands immediately when heated, would overflow if not placed in a cooler situation. The degree of nsion produced in different liquids, by similar elevations of tem-ture, varies very considerably. Thus water expands much more mercury, and alcohol more than water. This difference of nsibility is even sufficiently striking to appear in a remarkable ee when we immerse, in water heated to 150°, three equal glass els of the shape of thermometer tubes, containing the one mer-, the other water, and the third spirit of wine. The spirit will a to escape from the aperture of the vessel, before the mercury ascended far in the stem.



t must be obvious, however, that we cannot determine, in this the true amount of expansion in any fluid, because the containing vessel has, at the same time, its capacity enlarged. Hence the real nsion of the fluid exceeds the apparent; and, in order to know rue amount of expansion in the liquid, we must correct the rimental result by taking into account the expansion of glass. In determining the ation of mercury, MM. Petit and Dulong avoided the necessity of this correction, ollowed a method founded upon a hydrostatical principle—*viz.*, that when two ns of liquid communicate by a horizontal tube, the vertical heights of their sur-are in the inverse ratio of their densities. Surrounding, therefore, one of the ns with ice, and raising the other to any known temperature, it was found to be ient, in order to obtain the absolute dilatation, to measure the height of each m.*

he following is a description of the instrument employed and the principles on h its action depends :—

et A B C D be a tube bent twice at right angles, as represented in the diagram, xpanded into a cup-shaped vessel towards each upper extremity, the horizontal tube of connexion being exceedinly fine. Each vertical arm of the tube is seen to be immersed in a cylindrical glass vessel, the use of which is to contain liquids of definite temperature, in order that the upright arms may be heated to a corresponding degree. From this arrangement it follows that the rate of expan-



of a fluid may be estimated, independently of any disturbance, from expansion e glass. It is a well known proposition in hydrostatics, that the columnar

* "Ann. Ch. et Ph.," vii. p. 127, or "Ann. of Phil." Second Series, vol. xiii.

height of liquids of different densities, in equilibrio, under the same degree of pressure, is in an inverse ratio to the density of those liquids. Supposing, then, mercury to be poured into the vessel A B C D, the liquid will rise to the same level in the branches, A B and C D,—if the temperature be equal. If, however, the stem, A B, be heated to a degree which may be represented by t, whilst the stem, C D, is heated to a different temperature, which may be represented by t', the mercury will rise in the second branch higher than in the first. Let h stand for the columnar height of mercury in the lower branch, and h' for the columnar height of the same in the higher branch.

If, now, d' and d represent the densities of mercury at the temperatures t' and t, p the pressure of liquid referred to unity of surface, and exercised upon the horizontal plane, traversing the axis of the tube, B C being equal for all that plane, then

$$p = ghd = gh'd', \text{ therefore } hd = h'd';$$

or, the same weight of mercury occupying a volume in A B, where the density is d, should occupy in D C, where the density is d', a volume V', yielded by the equation $P = gVd = gV'd'$; whence $Vd = V'd'$, and from the equation $hd = h'd'$ and $V : V' :: h : h'$ is deduced $\frac{V' - V}{V} = \frac{h' - h}{h}$. But $\frac{V' - V}{V}$ is the fraction representing the augmentation with increase of temperature, experienced by the unity volume of mercury; when its temperature at t becomes t', this fraction of dilatation of mercury for $(t' - t)$ degrees will be $\frac{h' - h}{h}$, and the coefficient of dilatation $\frac{h' - h}{h\,(t' - t)}$. Whence it follows that the investigation of determining the total expansion of a liquid for a definite number of degrees, by means of this instrument, resolves itself into the exact measurement of the columnar fluid-levels at h and h', for the temperatures t and t'.

The most recent investigations concerning the dilatation of liquids have been made by M. Isidore Pierre and M. Kopp, who confirm the previously-existing belief, that, with the exception of mercury, the dilatation of liquids follows an exceedingly irregular and complicated progression.

It is, however, probable that a suggestion thrown out by M. Gay Lussac may, if carried into practice, tend to indicate some precise law of liquid expansion. The rate of expansion for all gaseous bodies is very nearly alike. Now gases possess nearly the same molecular state as to aggregation; *not quite the same*, as is proved by the different amounts of force necessary to liquify and solidify those gases capable of assuming such conditions, and the non-condensibility of others,—to which proof may be added the slight discrepancy in their coefficients of expansion. Liquids, however, are very differently circumstanced: the molecular forces which hold their particles together vary within the limits of a very wide range. M. Gay Lussac, therefore, suggests that in order to deduce a law of expansion for liquids, they should be examined under equal conditions of molecular aggregation. Now, exactly at the boiling point, the molecular aggregation of a liquid, determining the condition of liquidity, is overcome; hence, by taking a series of liquids, heated nearly to their boiling point, and cooling, through an equal number of degrees, the indications of some general law might probably, M. Gay Lussac thinks, be arrived at. Nor have his speculations been altogether without foundation, as the accompanying tabular view will demonstrate.

Alcohol boils at 173° F., water at 212° F.; sulphuret of carbon at 134° F., and sulphuric ether at 96·5° F. Taking 1·000 volumes of each at their boiling

points, and cooling through a definite number of degrees, the following results were obtained:—

By cooling through	Water contracts	Alcohol contracts	Sulphuret of Carbon contracts	Ether contracts
18°	6·61	11·43	12·01	16·17
36°	13·15	24·34	23·80	31·83
54°	18·85	34·74	35·06	46·42
72°	24·10	45·63	45·77	58·77
90°	28·56	56·02	56·28	72·01
108°	32·42	65·96	66·21	

It will be observed that the accordance between the alcohol and sulphuret of carbon for all the decrements of temperature, forming the subject of experiment, is marked, showing that there exists some kind of accordance between the molecular states of these two liquids, notwithstanding the difference of their boiling points. M. Isidore Pierre has drawn up extensive tables on the basis of that just given, and from which it appears that a nearly equal contraction, from the boiling point downwards, is manifested by (1) fusel oil, pyroxylic spirit, and alcohol; (2) bromide of ethyl and bromide of methyl; (3) iodide of methyl and iodide of ethyl; (4) acetic ether and acetic methyl ether; (5) butyric ether and butyric methyl ether. This equality of contraction, however, from the boiling-point downwards, does not extend to all groups of liquids containing a common element, united with others of different isomorphous groups—for example, chloride of phosphorus and chloride of arsenic; but it would seem to be confined to the ethyl and methyl series. Moreover, in each group of liquids, the difference of contraction increases constantly in the same direction, proportionate directly to the sinking of the temperature below the boiling point. In some cases this variation of contraction is of very considerable magnitude; thus, for example, in the group to which chloride and bromide of silicon belongs, it amounts to half the total expansion. Finally, in each group, the liquid of lowest boiling temperature manifest the greatest amount of expansion and contraction. Such are the chief generalizations arrived at by M. Isidore Pierre.* M. Kopp† has more recently applied himself to the same difficult investigation; but as this philosopher's generalizations are not yet complete, and the minutes of his researches are voluminous, I must refer to the original papers, wherein the information is conveyed.

The expansion of *aëriform bodies* may be exemplified by holding near the fire a bladder half filled with air, the neck of which is closely tied, so as to prevent the inclosed air from escaping. The bladder will soon be fully distended, and may even be burst by continuing and increasing the heat. All aëriform bodies, when deprived of moisture, and even condensable vapours, when not in contact with the liquids from which they have been produced, undergo nearly the same expansion or contraction, at all temperatures hitherto tried, by similar additions or subtractions of heat. Indeed, until the recent investigations of M. Regnault on this interesting subject, the proposition was universally accepted, that the amount of expansion and contraction of all gases for equal degrees of temperature was absolutely the same, being for the 180° of Fahrenheit's thermometer, between 32° (the freezing point) and 212°, about the $\frac{1}{480}$th

* "Annales de Chimie et de Physique," third series.

† "Pogg. Annal." 72, 1, and 223, abstracted in "Annal. de Chim. and Pharm." 64, 212.

of their volume at 32 for every degree—that is to say, 180 × $\frac{1}{480}$ths, or 0·375ths increase on the total bulk at 32° Fah. Mr. Dalton, who was the first to commence this important investigation, adopted the fraction $\frac{1}{483}$ as the coefficient of gaseous expansion; but MM. Petit and Dulong, who subsequently repeated the necessary experiments, adopted $\frac{1}{480}$ instead,* and their views were universally received until a Swedish natural philosopher, M. Rudberg, announced that the coefficient was too high, and that it was more nearly represented by the fraction 0·364 or 0·365 on the total increase of a volume of gas at 32° Fah., when heated to 212° Fah. It would appear that Mr. Dalton, as well as MM. Gay Lussac, Petit, and Dulong, had been led into error, owing to their not having taken sufficient care to dry the gases upon which they operated; hence the total amount of expansion recognized was partly due to the gas itself and partly to the water contained in the gas. In the year 1842, M. Regnault applied himself to a re-consideration of this subject, adopting two series of experiments founded on two different principles. In the first series the dilatations were not measured directly, but calculated by reference to variations in the elastic force of the gases operated upon. In the second series, the augmentation of volume occurring between 32° and 212° Fah. was directly measured; the same volume of gas being constantly used, and submitted to one unvarying pressure. These admirable researches of M. Regnault have led to the adoption of ·3665 or ·3670 as the total amount of expansion between 32° and 212° on the original bulk of air at 32°, being $\frac{11}{30}$ths of each centigrade degree, or $\frac{1}{491 \cdot 13}$ of a degree of Fahrenheit.

Laws of Expansion.—Such was the result arrived at for atmospheric air; other gases were found to yield slightly different rates of expansion: hence the proposition that all gases expand equally, for equal increments of temperature can be no longer accepted. Indeed there is one fact which, if duly weighed, might have rendered this proposition suspected. Certain gases, it is known, are condensible, others not; and amongst those which are, the force necessary to accomplish condensation varies within limits which are very wide. Now, if there be recognizable a difference in the molecular powers of gases at this end of the scale, it would seem *à priori* that there should be conversely a difference also at the other. M. Regnault's experiments bear out the supposition; he finds the coefficients of expansion to vary for different gases. The subjoined table manifests some of these variations, which will be seen to be greater in proportion as the particular gas under examination is readily condensible:—

Hydrogen	0·36613
Atmospheric air . . .	0·3670
Carbonic oxide . . .	0·36688
Carbonic acid . . .	0·37099
Protoxide of nitrogen . . .	0·37195
Cyanogen	0·38767
Sulphurous acid . . .	0·39038

Anterior to the investigations of M. Regnault on this subject, two fundamental laws were recognized in the theory of gaseous expansion.

These laws are as follow:—

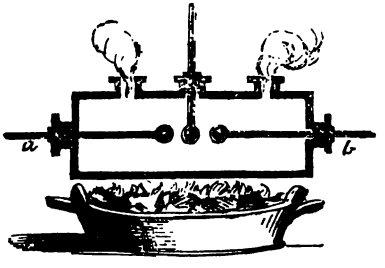
1. All gases dilate to the same extent between equal limits of temperature.

* "Ann. of Phil." new series, [illegible]

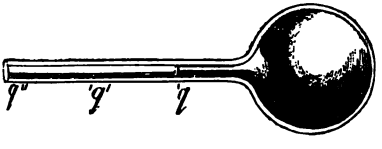
2. The dilatation of the same gas between the same limits of temperature is independent of its primitive density.

The first of these laws, as we have seen, is at variance with the results of M. Regnault. The second is no less at variance. Nevertheless, these laws, although not absolutely true, are sufficiently near the truth to justify their retention in chemical works. Probably they would be absolutely free from all error if applied to gases distant by an equal number of degrees from their respective points of condensation; hence the fraction $\frac{1}{480}$ of their bulk at 32° may be used to indicate the expansion suffered by all gases for every degree between 32° and 212° Fah.

Having enumerated the laws of the expansion of gaseous bodies, it will be desirable to indicate the means by which these laws have been deduced. A rectangular box of tin-plate, or copper, is supplied with five orifices—three superiorly, one at either extremity. The middle one above gives entrance to a thermometer, the stem of which is packed in a collar; the two remaining apertures above are intended for the escape of vapour. The terminal aperture *a* also gives entrance to a thermometer, whilst the aperture at *b* is fitted up with a bulbed glass and stem, constituting the immediate apparatus, by means of which the rate of expansion is to be determined. The tin vessel contains oil, which admits of being heated by means of the small furnace represented in the woodcut, to the degree necessary for the success of the experiment.



It will be evident that, by means of this disposition, a volume of air contained in the bulb of the glass tube passing through *b* will be expanded into a larger volume so soon as heat is applied to the tin vessel. It remains to ascertain the rate of expansion, which is easily effected by a register of quicksilver in the stem of the tube. That is to say, supposing a globule of quicksilver at the beginning of the experiment to stand at *q*, the same globule will be driven towards the open end of the tube by every subsequent increment of temperature in the direction of *q′ q″*.



It will be readily conceived that a knowledge of the exact amount of expansion to which gases are subject for given ranges of temperature possesses more than a theoretical interest. Although the expansion of all gases be not equal for equal degrees and the same range of temperature as the experiments of M. Regnault have proved, yet the approach to equality is such, that for all practical calculations the proposition of such equality may be assumed. Perhaps the fraction $\frac{1}{491}$ is the coefficient of expansion for each degree between 32° and 212° Fah., the most in accordance with experiments as a general means of observation. I shall, therefore, employ it henceforth in the illustrations which follow. On this assumption, it appears that 491 volumes of a gas at the temperature of 32° Fah. expand one volume for every degree of Fahrenheit's

scale between 32° and 212°; that is to say, if this standard measure of gas b to 212°, it will have expanded to 671 volumes. Furthermore, experiments ha that the rate of expansion at temperatures above 212°, and below 32°, is accordant with the range between, that the coefficient of expansion may be co universally as represented by $\frac{1}{491}$. Hence the correction of gaseous expan contraction involves the adding or the subtracting so many $\frac{1}{491}$ths of the such gas at 32°, as there are inequalities of temperature between 32° and the which the experiment is conducted. Thus, suppose that a graduated tube 100 measures of gas at the temperature of 32°, and it were desired to ascer many volumes it would occupy at 42°. Here the difference between 32° and 10 degrees, the 100 measures of gas will have expanded $\frac{10}{491}$ths of 100, or $\frac{10}{49}$ which must be added to the original 100 measures. But 100 added to $\frac{10}{491}$ the quantity 102·037, which is the amount of expansion sought.

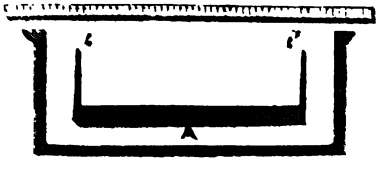
It frequently happens that the problem has to be solved of reducing a gas temperature to another temperature, neither of which is 32°. This may b plished without the preliminary trouble of finding the volume at 32°, by int into the proportion the standard measure 491. It has already been sho 491 volumes of gas at 32° expand one volume for every degree of increme 212° Fah.; and whatever the quantity of gas operated upon, the expansion same ratio. Now the rate of expansion of the standard measure 491 volume given number of degrees is simply ascertained by mere addition; whence that the volumes at the two temperatures are to each other as the standar (491 at 32°) increased by the amount of expansion due to the temperatur supposing a certain bulk of gas to occupy 130 volumes at 75°, what bulk occupy at 42°? Here the first questions to be solved are, what bulk w standard measure of gas (491 volumes at 32°) occupy at 75° and 42° resp These questions are readily solved by adding to 491 the respective difference 75°, and 42°, and 32°. Now the difference between 32° and 75° is 43°, and the between 32° and 42° is 10°. Hence we have (491 + 43) = 534 and (491 + 1 as the respective bulks of the standard measure of gas (491 volumes at 3 heated to 75° and 45° respectively: and calling the unknown volume V, we following proportion:—

$$V : 130 :: 501 : 534;$$

$$\text{and } V = \frac{130 \times 501}{534} = 119{\cdot}17;$$

or, 130 volumes of gas at 75° would occupy 119·17 volumes at 42°.

The expansion of solids may be made apparent by heating a rod of iron, length as to be included, when tween two points, and the di which is such as barely to allow through an iron ring. Wher it will have become sensibly lon it will be found incapable o through the ring.



These operations readily de the general truth: but the amo pansion undergone by a metallic bar within a definite range of temperature is as by a contrivance of the following description:—A represents a bar of metal, t

of which has to be estimated. The bar is surrounded by a heated bath, and is supplied with two vertical indices (i i'), one attached at right angles to either extremity. From which arrangement it follows, that in proportion as the bar expands, the indices will diverge; and that the amount of divergence being determined by means of the graduated rule figured above, the total amount of expansion undergone by the bar will be appreciated.

The linear expansion of a metallic bar being known, its total or cubic expansion may be easily deduced from the following consideration. If the material, instead of being in the form of a bar, were moulded into an accurate cube, then it follows that the total expansion of the bar would be equal to the total expansion of the cube; but the latter would be equal to the cube of the linear expansion of one of the edges of the cube. In other words, the total expansion of a bar is equal to the total expansion for the same thermal increment of a cube of homologous sides. Hence the coefficient of linear expansion of a bar cubed is equal to the cubic expansion of a bar. To illustrate this truth, let v be the volume of a cold metallic bar, v' its volume when heated. Now, as the expansion takes place according to the same ratio in every part of the bar, the latter, when hot, will have the same shape and the same relative dimensions as it had when cold. Hence we establish the proportion

$$v : v' :: 1 : (1 + d)^3; \text{ or,}$$
$$v : v' :: 1 : 1 + 3d + 3d^2 + d^3.$$

But in the generality of these cases d is so minute a fraction that $3d^2v$ and d^3v are almost inappreciable, and need not be taken cognizance of. Hence we may in most cases be content with indicating the total increment of cubic expansion by $3d$: neglecting $3d^2$ and d^3 altogether. In other words, the linear expansion of a bar multiplied by 3 represents almost exactly its cubic expansion.

To show how safely $3d^2$ and d^3 may be omitted, it is only necessary to convert these literal coefficients into numerals, applying them to some specific case. Thus, supposing a rod, or tube, of flint glass to be 20 inches long at 32°, and that, when heated to 212°, its linear amount of expansion is $\frac{1}{1248}$th of its length *at* 32°, or $\frac{1}{1248}$th of 20 inches $= \frac{20}{1248}$th of an inch, or in decimals, 0·001602. Reducing now our literal coefficients to their corresponding numerals, we have

		Inches.		
1	$=$	20		
d	$=$	$\frac{20}{1248}$	$=$ 0·00160200000	of an inch.
$1 + d$	$=$	$20 + \frac{20}{1248}$	$=$ 20·00160200000	"
$3d$	$=$	$\frac{60}{1248}$	$=$ 0·00480600000	"
$3d^2$	$=$	$\frac{1200}{1557504}$	$=$ 0·00007699200	"
d^3	$=$	$\frac{8000}{1943784992}$	$=$ 0·00000123540	"

from an examination of which the extremely small value of $3d^2$ and d^3 may be recognized.

Linear Expansion of Solid Bodies, when heated from 32° to 212° *Fah.*

Black marble (Lucullite)	0·00035300	$= \frac{1}{2833}$	Dunn and Sang.
Carrara marble	0·00083700	$= \frac{1}{1193}$	
White glass in tubes	0·00089694	$= \frac{1}{1115}$	Lavoisier and Laplace.
Flint glass	0·00081166	$= \frac{1}{1248}$	
Earthenware	0·00083000	$= \frac{1}{1200}$	Dalton.

Linear Expansion of Solid Bodies, when heated from 32° to 212° Fah.

Brown Fayence	0·00040000	$= \frac{1}{2400}$	
Antimony	0·00108333	$= \frac{1}{923}$	Smeaton.
Bismuth	0·00139167	$= \frac{1}{719}$	
Zinc (cast)	0·00294167	$= \frac{1}{340}$	
—— (hammered)	0·00310833	$= \frac{1}{322}$	
Malacca tin	0·00193765	$= \frac{1}{516}$	Lavoisier and Laplace.
Lead	0·00284836	$= \frac{1}{351}$	
Iron wire	0·00123504	$= \frac{1}{812}$	
Copper	0·00171733	$= \frac{1}{582}$	
Brass wire	0·00193337	$= \frac{1}{517}$	Smeaton.
Silver	0·00190868	$= \frac{1}{524}$	Lavoisier and Laplace.
Gold	0·00155155	$= \frac{1}{681}$	
Platinum	0.0009918	$= \frac{1}{1008}$	Troughton.
Palladium	0·0010000	$= \frac{1}{1000}$	Wollaston.

Anomalous Liquid Expansion.—By this term may be indicated the peculiar rate of expansion assumed by liquids resulting from the compression of gases. Philosophers have been in the habit of stating that gaseous bodies are those which of all others undergo the greatest amount of expansion and contraction for equal rates of temperature. The liquids, however, now treated of, at least many of them—perhaps all—depart widely from the law. Thus liquid carbonic acid is, for equal increments of heat, considerably more expansible than air; when heated from 32° to 86° Fah., twenty volumes expand to twenty-nine, which is about five times the rate of atmospheric dilatation.* Liquid sulphurous acid, and liquid cyanogen, according to Kemp, follow a corresponding anomalous law, but not to the extent of carbonic acid.

On reviewing the labours of philosophers who have investigated the subject of rate of expansion in solids, it will be seen with regret that no general principles have been deduced—no law arrived at. Nor is this, perhaps, a matter of surprise, when we consider the variation of molecular constitution to which non-crystalline solids are subject, although their general physical appearance remain the same. Thus all malleable metals are subject to ever-varying dimensions, according as they may have been hammered more or less; and all fusible metals are subject to the same variation, according to the rapidity with which they are cooled.

A similar remark applies to the errors attendant on correct determinations of the specific heat of solids. Thus Regnault has mentioned† that soft steel, the density of which at 14° C. is 7·8609, possesses a specific heat of 0·1165; whilst the specific heat of hard steel, whose density is 7·7982, rises to 0·1175. That the specific heat of soft bell-metal, having a density of 8·6843, is 0·0862; whilst the same metal, hardened to the density of 8·3797, possesses the specific heat of 0·0838.

Theory points to crystalline bodies as the solid materials from an examination of whose expansive ratios some general law is hereafter to be deduced. An investigation of this kind was first undertaken by Mitscherlich ‡ in whose steps followed M. Fresnel ;§

* Theorier, "Ann. Chim. et Ph." lx. 437.
† "Pogg. Annal." 42, 39.
‡ "Pogg.," i. 130; ii. 137.
§ "Bull. des Sc. Mathem.," 1824, 100.

more lately, Messrs. Playfair and Joule,* to whose respective communications the r is referred.

his property of metals has been applied to a variety of useful purposes. The iron or *tire*, as it is called, of a carriage-wheel, being purposely made a little smaller the wooden circle, is enlarged by heat so as to embrace the latter; and being then nly cooled by throwing water upon it, is again contracted, and becomes immovably

An ingenious use of the same principle was made several years ago, at Paris, by olard, in restoring to the perpendicular two opposite walls of the Museum of Arts Ianufactures, which had been pressed outwards by the incumbent weight. A r process has been had recourse to in effecting the restoration of the Cathedral at gh. Through holes in the walls, opposite to each other, several strong iron bars introduced, so as to cross the apartment, and to project outside the building ently to allow strong iron plates, or *washers*, to be screwed upon their ends. The rere then heated, and the iron plates screwed up. On cooling, the bars contracted, rew the separated walls nearer together; and this was repeated till the walls had ed their perpendicular position.

ie expansion of metals produces important effects in various mechanical instru-, especially in clocks; for a pendulum vibrating seconds will, by a change of rature equal to 30° Fah., alter its length about $\frac{1}{5000}$ part, which is sufficient to e its rate of going eight seconds of time per day.

mpensation Pendulums, and Balances.—Various plans have been had se to for obviating the errors attendant upon the elongation and contraction of ndulums of clocks. The simplest, and per-he best plan, when very large clocks are con-, consists in making the pendulum-rod of wood, r varnished. The inequalities of length atten-pon variations of temperature are thus in a great re avoided; wood being susceptible of these s to a very slight extent. Except the wood roughly seasoned, however, and the coat of h be accurately laid on, variations of another rise, due to the absorption of atmospheric re; hence, except for very large clocks, the rment of wooden pendulum-rods cannot be nended.

other means of avoiding this source of error gridiron pendulum, as it is technically called rvention of Harrison. This form of pendulum rarely employed in England, although it is nly used abroad, not exactly in its primitive but slightly altered and improved. The im-gridiron compensation pendulum will be tood by reference to the accompanying at.

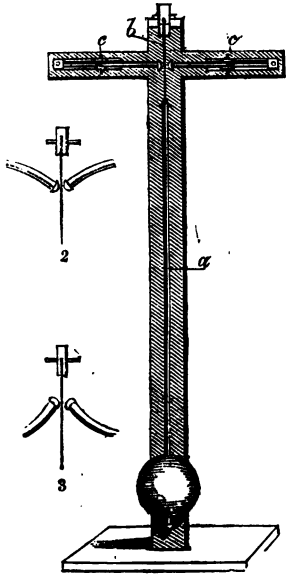
e compensating part of the instrument, re represented, consists of five vertical ttached to each other in the gridiron form, in a manner to be presently

* "Qu. Jour. of Chem. Soc." i. 121.

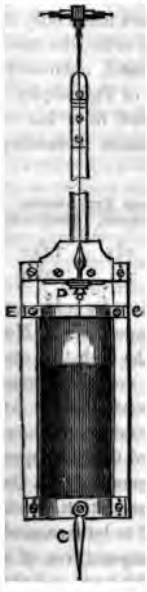
described. Of these rods, three (Nos. 1, 3, and 5) are of steel, and two (Nos. 2 and 4) of zinc. The steel rods 1 and 5 are securely fastened above to the brass cross-piece A *a*, and below to another brass cross-piece of similar kind, B *b*. The central steel bar is not attached to either of these cross-pieces; but perforating the lower one, it is fixed to the pendulum-weight, and at its upper extremity is attached to a short brass cross-piece, which also serves as the point of attachment for the upper ends of the zinc rods 2 and 4, the lower ends of these being fixed to the cross-piece B *b*. The total expansion of zinc for a given range of temperature exceeds that of steel by more than double; hence, in the above instrument, the mutual ratio of such expansion between the two metals is represented by an aggregate length of steel bar, which expands equally, for equal temperatures, to an aggregate length of zinc bar; and in proportion as this ratio is accurately maintained, so will be the accuracy of adjustment. Theoretically, it is conceivable that bar No. 3 should be pushed as far downward as the zinc bars are pushed upward; but in practice this accuracy is seldom attained.

In the original gridiron pendulum of Harrison brass was used instead of zinc for the upward expansion; but in this case nine bars were necessary instead of five—the difference of expansion between steel and brass being less than that existing between steel and zinc. A third description of compensation balance depends for its construction on the same principle as Bregult's thermometer, and the compensation balance spring of chronometers, presently to be described.

Let *a* represent a metallic pendulum-rod, suspended in the usual manner by a thin metallic slip to the fixed point *b*. Let *c c* represent two compound slips or stops, each formed of two plates, one of brass, the other of steel—the brass aspect being uppermost. These compound slips being fixed at the end furthest removed from the pendulum, and free to move at the other end, the result will be as follows:—When the temperature is elevated the pendulum-rod will be elongated, and were there no compensating adjustment, the rate of going of the clock would be retarded; but the same elevation of temperature affects the stops *c c*, causing the brass portions of them to expand more than the steel portions, and producing in each a curve, the convexity of which looks upward, as represented in the woodcut (2), the virtual effect of which is to shorten the pendulum. The effect of diminishing temperature will obviously be the converse of the preceding, and will be represented by the woodcut (3). Perhaps, however, the most usual contrivance had recourse to for the purpose of equalizing the effective length of a pendulum, under varying temperatures, is that of making the pendulum-weight a mass of quicksilver, which, being placed in a glass jar of proper dimensions, can be so adjusted as to expand upwards in the same ratio as that in which the pendulum-rod elongates. The mercurial pendulum (see next page) is now almost exclusively used in this country. It was invented, in 1722, by our countryman Graham, and is represented by the following sketch:



The compensation balance, which is the principal distinctive feature of the modern chronometer, is represented by the accompanying woodcuts, which illustrate the two varieties of this interesting piece of mechanism.



The semicircular pieces which form the rim of the balance consist, in both the instruments here represented, of a very thin piece of steel, with an outer rim of brass firmly attached to and forming one

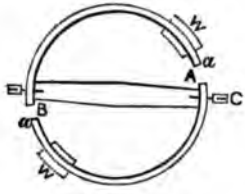


Fig. 1.

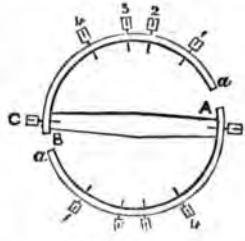


Fig. 2.

piece with it. The manufacture of these compensation balances is exceedingly curious. A circular piece of steel, of the size of the intended balance, being accurately turned, a small pivot-hole is made through the centre. It is then immersed into fused brass, with which it becomes accurately covered. Subsequently the brass is filed away from the sides, and partially from the edge, in such a manner that only a ring of brass remains firmly attached to the steel at every point; the whole is then carefully condensed by means of hammering or burnishing, the steel is turned away from the centre and the brass externally, so as to leave a thin compound ring, of which the brass part is about twice the thickness of the steel part. During this operation the steel is not entirely removed from the centre—a thin portion being left, out of which is cut the bar A B. The balance is completed by removing the superfluous parts of this transverse piece of steel, and cutting through the compound ring at *a a*. The balance is next adjusted, which is either accomplished by sliding weights, as in fig. 1, or by a number of small screws, as in fig. 2, which admit of being screwed in or withdrawn according to circumstances. The screws C C, called *mean-time* screws, regulate, by being screwed in more or less, the rate of the chronometer, but have nothing to do with the compensation for changes of temperature. This is effected spontaneously by the very nature of the balance itself, on the principle that brass and steel expand unequally for equal temperatures; the compound rim curving inwards, and thereby diminishing the centrifugal force of the balance when the balance-spring is relaxed by heat; or expanding, and thereby producing the contrary effect, when the spring is braced by cold. The proper situation of the weights W W, or the regulating screws 1, 2, 3, 4, is ascertained by experiment; the amount of compensation being greater in proportion as the weights are nearer to the free ends of the rim in the balance represented by fig. 1, while in the other form the like effect is produced by making the screws project more or less. Finally, the whole balance spring is in many cases protected from atmospheric agencies, and the steel portion of it protected from rust, by covering it with a thin layer of gold by the electrometallurgic process. This process is due to the ingenuity of Mr. Dent, who has also introduced the improve-

ment of making the balance spring of *glass*; the only disadvantage in the use of which being the difficulty of making this delicate appendage with certainty.

The degree of expansion is not the same for all solids, and even differs materially in substances of the same class. Thus, the metals expand in the following order, the most expansible being placed first: zinc, lead, tin, copper, bismuth, iron, steel, antimony, palladium, platinum. The experiments of Petit and Dulong ("Annals of Philosophy," xiii. 164) tend to show that unequal degrees of expansion are produced in a bar of metal by a succession of similar increments of heat; the rate of expansion increasing with the temperature, as appears from the following table:—

Temperatures measured by Expansion of Air.	Expansions in bulk of Iron.	Expansions in bulk of Copper.	Expansions in bulk of Platinum.	Linear Expansions. Iron.	Linear Expansions. Copper.	Linear Expansions. Platinum.
0° to 100° cent. give . . .	$\frac{1}{252}$	$\frac{1}{194}$	$\frac{1}{377}$	$\frac{1}{846}$	$\frac{1}{582}$	$\frac{1}{1131}$
0° to 300° cent. (mean) . .	$\frac{1}{227}$	$\frac{1}{177}$	$\frac{1}{363}$	$\frac{1}{681}$	$\frac{1}{531}$	$\frac{1}{1089}$

The expansion of bodies by heat, and, conversely, their contraction by cold, are functions not only of theoretical interest, but of the highest practical importance. Not only is a correct knowledge of this amount of expansion necessary to the architect and engineer, but the greater number of our instruments for indicating and measuring temperature depend upon an application of the laws of expansion and contraction. An instrument may be adapted merely for indicating a difference of temperature, without expressing the amount of such variation: such instruments are termed thermoscopes. Other instruments are adapted not only to indicate a difference of temperature, but the amount of that difference, referred to some conventional standard of graduation. Such instruments are termed thermometers when the temperatures intended to be measured by them are low; pyrometers when they are destined to measure temperatures of a higher range. Strictly speaking, the difference between the two is arbitrary, and the double name seems unnecessary. It is generally, however, understood that every instrument intended for the measurement of temperatures above the boiling point of mercury, 662° Fah., is a pyrometer.

A description of the different varieties of thermoscopes, thermometers, and pyrometers, will be given hereafter. In this place it is merely desired to discuss the conditions necessary to be possessed by a thermo-expansive material, in order that it may be adapted to the formation of heat-measuring, or heat-indicating instruments.

Inasmuch as solids, liquids, and gases, are all subject to the general law of expansion by heat and its converse, there does not appear any theoretical *à priori* objection to the adoption of either; nevertheless, it will be seen, on consideration, that the thermometric range of any given liquid is limited by the solidifying or freezing point of such liquid at one extremity of the scale, and its boiling point at the other; for which reason liquids are unadapted to measure by their amount of dilatation the existence of the higher temperatures—in other words, they are inapplicable to the purpose of pyrometers, for which latter, either solids of great infusibility or gases must be employed. It happens, nevertheless, that by far the greater number of thermal phenomena, presenting themselves in ordinary philosophical investigations, are not above the degree of 662° Fah., or that of the boiling point of mercury, and not below the freezing-point of the same, which is, in round numbers, — 40°, or 40° below zero. Hence the expansion and contraction of mercury, in a graduated glass tube, under the name of the mercurial thermometer, becomes the most usual standard of thermometric comparison. If mercury were endowed with a freezing-point lower than — 40°, to an extent commen-

surate with the wants of philosophers, there seems no reason why any other liquid than mercury should be employed in thermometers; but occasionally temperatures have to be measured which are lower than − 40°. Hence, some liquid must be employed that is capable of retaining its fluid state far below this temperature. Alcohol is the fluid then adopted. Pure alcohol has never been frozen; hence there should seem no limit from that cause in the downward scale of indication, and it answers the intended purpose very satisfactorily. In conducting certain specific lines of research, thermometers filled with other liquids than mercury or alcohol have been occasionally employed by philosophers; indeed, every liquid may be employed as a medium of thermometric measurement between the limits of its freezing and boiling point, with the sole exception of water, which, on account of a peculiarity of expansion and contraction, to be detailed hereafter, is unadapted to the purpose.

Pyrometers and Thermometers.—The most celebrated pyrometer is that of Mr. Wedgwood; and although the instrument be incorrect, it is still worthy of a short notice. Mr. Wedgwood, in the course of his technical operations, had his attention directed to the contraction of clay when exposed to furnace heat. Imagining that the amount of contraction was proportional to the heat employed, the idea occurred of measuring high temperatures by estimating the amount of contraction undergone by an accurately formed wedge of clay. Supposing the first assumption to be correct, it is evident that the result would have been as Wedgwood anticipated; and that a clay wedge, which before heating exactly fitted a gauge, would after heating no longer fit the same gauge. Such is the principle of Wedgwood's pyrometer; the gauge of which is formed of two convergent metallic grooves in a vertical plane, and graduated. In proportion as the wedge sank deeper towards the apex of convergence of the grooves, so was it assumed that the heat to be estimated had been greater.

Even had the principle been correct, an almost insuperable difficulty would have interposed in the circumstance that no two specimens of clay are exactly of the same composition. But there is another objection, one of principle, and it is fatal to the accuracy of the instrument. A long continued and gentle heat is competent to effect the same amount of contraction as a short but violent heat. It may be well here to point out that the contraction of clay by heating is not, as it at first seems, an exception to the general law. Clay suffers contraction on account of the loss of water with which it is chemically combined.

A more accurate pyrometer is that invented by the late Professor Daniell, and which bears his name. It is founded on the principle of measuring the expansion occurring to a bar of metal, for the most part of platium or iron. Like the pyrometer of Wedgwood, it consists of two parts; one of which alone is subjected to heat, the other being a register, or measurer of dilatation. That portion of the instrument subjected to the effects of heat, consists of a block of black-lead crucible ware, into which, but not through it, is drilled a hole something longer than a metallic bar intended to be dropped into it. Supposing an observation to be made, the metallic bar is first placed in its black-lead sheath, and a cylindrical piece of porcelain introduced above. The intention of this porcelain cylinder is to act as an index, for which purpose it is fixed, by means of a platinum strap and porcelain wedge, loosely enough to admit of motion forwards as the iron presses against it, but with sufficient tightness not to slide back again. All that now remains to be done, is to measure, by means of a graduated scale, the amount to which the index has been thrust forward.

"When an observation is to be made, a bar of platinum, or malleable iron, is placed

in the cavity of the register, the index is to be pressed down upon it, and firmly fixed in its place by the platinum strap and porcelain wedge. The scale is then to be applied by carefully adjusting the brass rule to the sides of the register, and fixing it by pressing the cross-piece upon the shoulder, and placing the moveable arm so that the steel point of the radius may drop into a small cavity made for its reception, and coinciding with the axis of the metallic bar. The minute of the degree must then be noted, which the nonius indicates upon the arc. A similar observation must be made after the register has been exposed to the increased temperature which it is designed to measure, and again cooled; and it will be found that the nonius has been moved forward a certain number of degrees or minutes. The scale of this pyrometer is readily connected with that of the thermometer by immersing the register in boiling mercury, whose temperature is as constant as that of boiling water, and has been accurately determined by the thermometer. The amount of expansion for a known number of degrees is thus determined, and the value of all other expansions may be considered as proportional."—DANIELL'S ELEMENTS.

The accuracy of this instrument, it is evident, will be, *ceteris paribus*, in proportion to the equality of dilatation experienced by the metallic bar at different temperatures; but this not being strictly the case, the pyrometer of Daniell is open to the objection which applies to all thermometers.

The instrument has been successfully applied to the purpose of ascertaining the maximum expansion attained by any metal before undergoing fusion. In this way the following results were obtained :—

TABLE OF PROGRESSIVE DILATATION OF SOLIDS.—1000000 PARTS AT 62°.

	At 212°.	At 662°.	At Fusing Point.
Black-lead ware .	1000244	1000703	
Wedgwood ware .	1000735	1002995	
Platinum . .	1000735	1002995	1009926 maximum, but not fused
Iron (wrought) .	1000984	1004483	1018378 to the fusing point of cast iron
Iron (cast) . .	1000893	1003943	1016389
Gold . . .	1001025	1004238	1024376
Copper . . .	1001430	1006347	1024376
Silver . . .	1001626	1006886	1020640
Zinc . . .	1002480	1008527	1012621
Lead . . .	1002323	. . .	1009072
Tin . . .	1001472	. . .	1003798

The air thermometer of Pouillet* consists of a hollow platinum sphere communicating with an escape tube, through which the air presses in proportion as the heat applied to the hollow sphere. Although the principle of this instrument is simple, its practice is attended with many difficulties. So many precautions have to be taken, and corrections made, that its indications can scarcely be depended upon. By slightly varying this principle, a very ingenious air pyrometer has been contrived by M. Peterson. His apparatus consists of a platinum flask closed by a screw, but not absolutely air-tight. Thus prepared, the flask is taken from the source of heat and rapidly

* "Poggendorff's Annalen," 39, 367. "Pouillet's Elémens de Physique et de Météorologie," 3me Ed., tom. I., p. 351.

plunged under water, when the internal volume of air contracting, water rushes in between the screw threads to supply its place. The flask being now weighed, it is evident that the increase of weight due to the presence of water will be directly proportionate to the amount of air expelled; or, in other words, to the air's expansion due to heat. Hence the determination of the amount of heat ultimately resolves itself into a determination of the air expansion; and as air expands $\frac{1}{491}$th of its volume, at 32° for the increment of every degree on Fahrenheit's scale, the theoretical solution of the problem is easy, although certain practical difficulties intervene.

All the thermometric and thermoscopic instruments hitherto described have reference to the thermal variation in dimensions of solids, liquids, or gases; the most delicate indicator of temperature or thermoscope, however, is totally independent of this function, and derives its indications from an observance of the deflection of a magnetic needle. The full comprehension of the nature of this instrument must be postponed until the chapter on electricity, on the operation of which it depends; meanwhile it may be stated, however, that the alteration of temperature occurring in any body is always accompanied by electrical disturbance,—which electrical disturbance, if made to traverse a circuit parallel to a freely poised magnetic needle, the latter is more or less deflected; whence it follows, that the deflection of a poised magnetic needle becomes an indication of temperature. Unfortunately this very delicate instrument, although highly sensitive to changes of temperature, is not competent to indicate the amount of such change—hence it is a mere thermoscope, not a thermometer. By its inventor, Signor Nobili, this instrument has been termed the thermomultiplier: it has been much used by Signor Melloni in testing the presence or absence of thermal rays in luminous radiant matter.

M. Breguet has constructed a very sensible metallic thermometer, for temperatures between the freezing and boiling points of water,* by taking advantage of another thermic function, the unequal expansion and contraction of different solids.

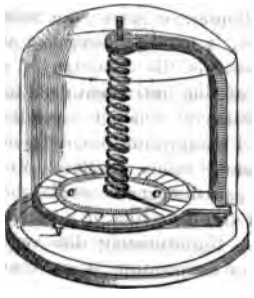
A good class-room experiment for illustrating this inequality of expansion is the following. Let there be provided two slips, or thin bars, one of iron, the other of brass—each about $\frac{1}{16}$th of an inch thick, about 2 inches wide, and 15 inches long. Let these two slips of equal size in every respect be now firmly rivetted together, and a compound slip formed, as represented by the woodcut *a*.

Exposed to ordinary atmospheric temperatures, a compound slip of this kind remains straight; but if it be heated, a curved form results, as shown in Figs. *b* and *c*, the convex side of the curve being in all cases the brass slip, whether the source of heat has been applied to the iron or the brass side of the compound slip.

The principle of Breguet's thermometer will now be readily apparent. It consists of a slip of silver and another of platinum, united face to face with solder, and coiled into a spiral, one end of which is fixed, while the other is connected with an index which moves over a circular graduated plate. Strictly, two metals only are sufficient for the purpose, platinum and silver for instance; but it has been found to be an improvement to employ three, and the instrument is now prepared by interposing between the

* "Ann. de Chim. et de Phys.," v. 312.

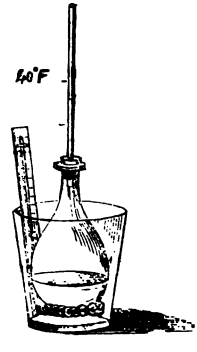
platinum and silver a metal of mean dilatability, such as pure gold. The unequal expansion of the metals causes the spiral to increase or diminish the degree of its curvature by variations of temperature; and the needle, being attached at right angles to the axis of the spiral, is thus made to traverse the graduated circle. Experiment has shown that the needle, for equal changes of temperature, moves over equal arcs, so that the instrument is comparable, not only with itself, but with others constructed on the same principle. Such was found to be its great sensibility, that, when inclosed in a large receiver, which was rapidly exhausted by the air-pump, it indicated a reduction of temperature from 66° Fah. to 25° (= 41°), while a sensible mercurial thermometer, similarly situated, fell only 3·6°. The appended woodcut further illustrates the nature of the instrument.



To the general law of the expansion of bodies by heat, and their contraction by cold, there are, however, several exceptions. Water by freezing is considerably increased in bulk; salts in the act of crystallizing expand; and some of the metals, as cast-iron, bismuth, and antimony, have their dimensions enlarged by congealing; but mercury and other metals follow the general law, and occupy less bulk when solid than when fluid.

The greater bulk occupied by ice than the water yielding it is but one exemplification of a general law to which the greater number of crystallizable bodies are subject—*i. e.*, they expand during the act of crystallization. In another respect the relations of water to temperature and bulk are remarkable, and without parallel. Not only does water expand at 32°, the freezing temperature, but some degrees above this, inasmuch as a portion of water acquires its greatest density somewhere between the degrees of 30° and 40° Fah., so that if brought to this temperature a portion of water expands, whether heated or cooled. This fact may readily be demonstrated by means of a simple apparatus.

Let a Florence oil flask be supplied with a tightly-fitting perforated cork, to which is attached a piece of glass tube, having a bore from the eighth to the tenth of an inch in diameter, and a length of about two feet.



Let the Florence flask be now propped upright by means of a ring of tow, or other convenient support, in a beaker or jar, to serve the purpose of a bath, and let water of the temperature of about 60° Fah. be poured into the tube until the flask and tube are nearly full. This disposition being made cold should be now applied to the Florence flask externally, by pouring water, containing a little ice, into the bath. Under these circumstances the level of the water in the tube will continue to fall until the thermometer indicates the temperature of the bath, and consequently of the water in the Florence flask, to be about 40° Fah. From this point it will be remarked that a continued application of cold occasions expansion; and this expansion through the eight degrees of decrement of temperature between 40° and 32°, is about equal to the expansion consequent on eight degrees of thermal increment; so that at 38° Fah. a

given weight of water occupies the same bulk as at 42°, at 37° Fah. the same bulk as at 43°, and in like manner for the remaining degrees.

This peculiarity in the expansion and contraction of water under thermal influence was first remarked by the Florentine academicians towards the latter end of the 17th century, and almost immediately after confirmed in England by Drs. Croune and Wallis, and Messrs. Hooke and Hunt.

For the sake of avoiding complication in directions for conducting the preceding experiment, the round number, 40° Fah., has been adopted as that at which a given weight of water attains its maximum contraction. In point of fact, however, it is exceedingly difficult to ascertain the exact degree, or fraction of a degree, at which this maximum condensation is accomplished. According to Crichton the degree is 42° Fah.,* whilst the experiments of Hallström place it at 39·4.†

More recently M. Despretz, having applied himself to this difficult investigation, arrived at the conclusion that water attains its maximum density at + 4° centigrade = 39·2° Fah. His results seem to indicate, moreover, that the downward rate of dilatation is more considerable than the upward rate. The difference, however, according to this philosopher, is very minute, and may be probably attributable to errors of apparatus or observation. The same philosopher also finds that sea water, and all saline solutions, have a maximum of density, and that this maximum of density sinks more rapidly than the point of congelation.‡

"The anomalous expansion of water by cold," remarks a modern philosopher,§ "is productive of some most important consequences in nature; for if water, like other fluids, went on diminishing in bulk, and therefore increasing in density, till it froze, large bodies of water, instead of being only superficially frozen in winter, would become solid masses of ice. Let us take a fresh-water lake as an example. The earth being warmer in winter than the air, the heat is withdrawn from the *surface* of the water by the cold breezes that blow over it, and the whole body of water has its temperature lowered to 40°, *which is the point of its greatest density*, and a temperature congenial to fish and other aquatic animals. The cold now continues to operate upon the surface of the water; but instead of diminishing its bulk, and rendering it heavier than the warmer water underneath, it expands and renders it *lighter;* so that, under these circumstances, a stratum of ice-cold water (at 32°) will be found lying upon a mass of warmer water beneath it (at 40°). The influence of the cold continuing, the surface of the lake will soon freeze, but the water immediately below the superficial coating of ice will be found comparatively warm; and as water is almost a non-conductor of heat, it will be a long time before the ice attains any thickness; and the whole body of water, if of any depth, can never freeze throughout. Indeed, it will be obvious that the retardation of freezing will be proportional to the depth of water which has to be cooled, and hence some very deep basins or lakes are scarcely ever covered with ice."

II. *Construction of the thermometer, founded on the principle of expansion.*—The thermometer is an instrument of so much importance, that it may be expedient to trace its history, and to explain the construction of the different kinds which are required in chemical researches.

The instrument employed by Sanctorio, to whom the invention of the thermometer

* "Ann. of Phil.," new series, v. p. 491. † "Ann. de Chim. et Phys.," xxviii. p. 90.

‡ Vide Original Monograph, by M. Despretz, "Ann. de Chim. et Phys.," t. lxx.

§ Professor Brande.

is generally ascribed, was of a very simple kind, and measured variations of temperature by the variable expansion of a confined portion of air. To prepare this instrument, a glass tube is to be provided, eighteen inches long, open at one end, and blown into a ball at the other. On applying a warm hand to the ball, the included air expands, and a portion is expelled through the open end of the tube. In this state the aperture is quickly immersed in a cup filled with any coloured liquid, which ascends into the tube as the air in the ball contracts by cooling. The instrument is now prepared. An increase of temperature forces the liquor down the tube; and, on the contrary, the application of cold causes its ascent. These effects may be exhibited alternately by applying the hand to the ball, and then blowing on it with a pair of bellows. By the application of a graduated scale the amount of the expansion may be measured.

The ball of the above instrument, it must be obvious, cannot be conveniently applied to measure the temperature of liquids. For adapting it to this purpose, a slight variation may be made in its construction. To prepare this instrument, a small spherical glass vessel is to be about one-sixth or one-fourth filled with any coloured liquid. The tube, open at both ends, is then to be cemented into the neck, with its lower aperture beneath the surface of the fluid. The expansion of the included air drives the liquid up the stem, to which we may affix a graduated scale, corresponding with that of a common mercurial thermometer. Other modifications have also been made by different philosophers. One of the most useful and simple consists merely of a tube of very small bore, from 9 to 12 inches long, at one end of which is blown a ball, from half an inch to an inch in diameter, which is afterwards blackened by paint, or by the smoke of a candle. A small column of coloured liquid, about an inch in length, is then introduced, by a manipulation similar to that already described. To fit the instrument for use, this column ought to be stationary, about the middle of the tube, at the common temperature of the atmosphere. The slightest variation of temperature occasions the movement of the coloured liquid; and a scale of equal parts measures the amount of the effect.

An insuperable objection, however, to the air thermometer, *as thus constructed*, is, that it is affected not only by changes of temperature, but by variations of atmospheric pressure. Its utility consists in the great amount of the expansion of air, which, by a given elevation of temperature, is increased in bulk about twenty times more than mercury. Hence it is adapted to detect minute changes, which the mercurial thermometer would scarcely discover; and, its expansions being uniform for equal additions of heat, it is better adapted than any liquid for becoming, when properly applied, an accurate measure of temperature.

An ingenious modification of the air thermometer has been invented by Mr. Leslie, and employed by him, with great advantage, in his interesting researches respecting heat. To this instrument he has given the name of the Differential Thermometer. Its construction is as follows:—"Two glass tubes of unequal length, each terminating in a hollow ball, and having their bores somewhat widened at the other ends (a small portion of sulphuric acid, tinged with carmine, being introduced into the ball of the longer tube), are joined together by the flame of a blowpipe, and afterwards bent nearly into the shape of the letter U, the one flexure being made just below the joining, where the small cavity facilitates the adjustment of the instrument. This, by a little dexterity, is performed by forcing, with the heat of the hand, a few minute globules of air from the one cavity into the other. The balls are blown as equal as the eye can judge, and from four-tenths to seven-tenths of an inch in diameter. The tubes are such

as are drawn for thermometers, only with wider bores; that of the short one, to which the scale is affixed, must have an exact calibre of a 50th, or a 60th, of an inch. The bore of the long tube need not be so regular, but should be visibly larger, as the coloured liquid will then move quicker under any impression. Each leg of the instrument is from three to six inches in height, and the balls are from two to four inches apart.

"A moment's attention to the construction of this instrument will satisfy us that it is affected only by the *difference* of heat in the corresponding balls; and is calculated to measure such difference with peculiar nicety. As long as both balls are of the same temperature, whatever this may be, the air contained in both will have the same elasticity, and, consequently, the intercluded coloured liquor, being pressed equally in opposite directions, must remain stationary. But if, for instance, the ball which holds a portion of the liquor be warmer than the other, the superior elasticity of the confined air will drive the liquid forwards, and make it rise, in the opposite branch, above the zero, to an elevation proportional to the excess of elasticity, or of heat." The amount of the effect is ascertained by a graduated scale, the interval between freezing and boiling being distinguished into 100 equal degrees. This instrument, it must be obvious, cannot be applied to measure variations in the temperature of the surrounding atmosphere, for the reason already assigned. It is peculiarly adapted to ascertain the difference of the temperatures of two contiguous spots in the same atmosphere; for example, to determine the heat in the focus of a reflector.

A differential thermometer has been contrived by Dr. Howard, resembling that of Mr. Leslie in its general form, but in which the degree of heat is measured by the expansive force of the vapour of ether or spirit of wine *in vacuo*. Directions for constructing it are given in the eighth volume of the Quarterly Journal of Science, p. 219. It is intended to be applied to the same purposes as that of Mr. Leslie, but is said to be more sensible to changes of temperature, and the movement of the fluid (ether tinged by a drop of tincture of cochineal) follows instantaneously the application of the heating cause, whereas in the air thermometer some time is required before the effect takes place.

Thermometers, filled with spirit of wine (a liquid which has not been congealed by any degree of cold hitherto produced), are best adapted to the measurement of very low temperatures, at which mercury would freeze. The amount of the expansion of alcohol, also, which exceeds that of mercury above eight times, fits it for ascertaining very slight variations of temperature. But it cannot be applied to measure high degrees of heat; because the conversion of the spirit into vapour would burst the instrument.

The fluid best adapted for filling thermometers is mercury, which, though it expands less in amount than air, or alcohol, still undergoes this change to a sufficient degree; and, in consequence of its difficult conversion into vapour, may be applied to the admeasurement of more elevated temperatures. As a considerable saving of expense will accrue to the experimentalist who is able to construct mercurial thermometers, I shall offer some rules for this purpose. In general, however, I should deem it preferable merely to superintend their construction, when wanted for delicate experiments, and to be satisfied, by actual inspection, that the necessary accuracy is observed; because much time must be unavoidably lost in acquiring the manual skill which is essential to construct them neatly.

Thermometer tubes may be had at the glass-house, and of most philosophical

instrument makers. In purchasing them, those should be rejected that are not hermetically sealed at both ends; because the smallest condensation of moisture, which must take place when air is freely admitted within the tube, is injurious to the accuracy of the instrument. A small bottle of elastic gum should be provided, in the side of which a brass valve is fixed, or a piece of brass perforated by a small hole, to be occasionally stopped by the finger. A blow-pipe is also an essential part of the apparatus; and, in addition to one of the ordinary kind, it will be found useful to have one which is supplied with air by a pair of double bellows, worked by the foot.

Before proceeding to the construction of the thermometer, it is necessary to ascertain that the tube is of equal diameter in different parts. This is done by breaking off both of the sealed ends, immersing one of them an inch or two deep in clean and dry mercury, and then closing the other end with the finger. On withdrawing the tube from the mercury, a small column of that fluid remains in it, the length of which is to be examined, by laying the tube horizontally on a graduated ruler.* By inclining the tube, this column may be gradually moved through its whole length; and if the tube be of uniform bore, it will measure the same in every part. Such a degree of perfection, however, is scarcely ever to be observed throughout tubes of considerable length; but, in general, a portion of the tube will be found perfect, of sufficient length for a thermometer, and this part is to be broken off.

On one end of the tube let the neck of the elastic bottle be firmly tied; and let the other end be heated by the flame of the blow-pipe, till the glass softens. The softened part must then be pressed, by a clean piece of metal, into the form of a rounded button; and to this the flame of the lamp must be steadily applied, till it acquires a white heat, and seems about to enter into fusion. To prevent its falling on one side, the tube, during this time, must be constantly turned round by the hand. When the heated part appears perfectly soft, remove it quickly from the lamp, and, holding the tube vertically, with the elastic bottle uppermost, press this last gently with the hand. The glass will be blown into a small ball, but not into one sufficiently thin for the purpose. To this the flame of the lamp must again be applied, turning it quickly round; and, on a second or third repetition of the process of blowing, the ball will be completely formed. The proportion of the size of the ball to the bore of the tube can only be learned by some experience.

To fill the ball, which has been thus formed, with mercury, the air must first be expelled, by holding it over the flame of an Argand's lamp, and then quickly immersing the open end of the tube in very clean and dry quicksilver. As the ball cools, the mercury will ascend, and will partly fill it. Let a paper funnel be tied firmly over the open end of the tube, into this pour a small portion of quicksilver, and apply the heat of the lamp to the ball. Any remaining portion of air will thus be expelled; and if the heat be raised so as to boil the mercury, the ball and stem will be filled with mercurial vapour, the condensation of which, on removing the ball from the lamp, will occasion a pretty complete vacuum. Into this vacuum quicksilver will descend from the paper cone; and the instrument will be completely filled. But, for the purpose of a thermometer, it is necessary that the mercury should rise only to a certain height in the stem; and a few drops may, therefore, be expelled by cautiously applying the heat of the lamp. To estimate whether the proper quantity of quicksilver has been left in

* If the tube be of an extremely small bore, the mercury will not enter, and must be drawn in by the action of the elastic bottle, and not by the mouth.

the instrument, immerse the ball first in ice-cold water, and then in the mouth. The space between these two points will comprise about 64°, or rather more than one-third of the whole space between the freezing and boiling points of water. If the empty part of the tube exceeds, in length, about three times the portion thus filled by the expanded quicksilver, we may proceed (when an instrument is wanted with a scale including only from 32° to 212°) to seal it hermetically, which is done as follows:—The part to be sealed is first heated with the blow-pipe, and drawn out to a fine capillary tube; the bulb is then heated, till a few particles of quicksilver have fallen from the top of the tube: at this moment another blow-pipe flame is directed on the capillary part of the tube, the heat is withdrawn from the ball, and the tube is sealed, at the instant when the mercury begins to descend. If this operation has been skilfully performed, so as to leave no air in the tube, the whole of the tube should be filled with quicksilver on holding the instrument with the ball uppermost.

To have very large degrees, the ball must bear a considerable proportion to the tube; but this extent of scale cannot be obtained without sacrificing, in some measure, the sensibility of the instrument.* The whole of the process of constructing thermometers neatly and accurately is connected with the possession of manual skill, which practice only can confer; and it is scarcely possible, without the most tedious minuteness, to describe all the necessary precautions and manipulations. These will readily suggest themselves to a person who carries the above instructions into effect.

In graduating thermometers, the first step consists in taking the two fixed points. The freezing point is ascertained by immersing, in thawing snow or ice, the ball and part of the stem; so that the mercury, when stationary, shall barely appear above the surface. At this place let a mark be made with a file. In taking the boiling point, considerable caution is required; and, for reasons which will afterwards be stated, attention must be paid to the state of the barometer, the height of which, at the time, should be precisely 29·8. A tin vessel is to be provided (for, according to Gay Lussac,† one of glass leads to erroneous results), four or five inches longer than the thermometer, and furnished with a cover, in which are two holes. Through one of these the thermometer stem must be passed (the bulb being within the vessel), so that the part at which the boiling point is expected may be just in sight. The other hole may be left open; and, the cover being fixed in its place, the vessel, containing a few inches of water at the bottom, is to be set on the fire. The thermometer will presently be wholly surrounded by the steam; and when the mercury becomes stationary in the stem, its place must be marked. The scale of Fahrenheit is formed by transferring the intermediate space to paper by a pair of compasses, and dividing it into 180°, the lowest being called 32°, and the highest 212°. The scale of other countries, however, differs considerably; but these variations do not prevent the comparison of observations with different instruments, when the freezing and boiling points of water are agreed upon as fixed data.

III. *The dilatations and contractions of the fluid in the mercurial thermometer are nearly proportional to the quantities of caloric which are communicated to the same homogeneous bodies, or separated from them, so long as they retain the same form.*

Thus the quantity of caloric required to raise a body 20° in temperature, by the mercurial thermometer, is *nearly* double that which is required to raise it 10°.

* Directions for constructing thermometers of great sensibility are given by the Chevalier Landriani, in the 7th Volume of the "Journal of Science," p. 183.

† 82 "An. de Ch." 174, and 7 "An. de Ch. et de Phys." 307.

Hence there appears to be a pretty accurate proportion between the increments or decrements of heat, and the increments or decrements of expansion in the mercury of a thermometer. On this principle, if equal quantities of hot and cold water be mixed together, and a thermometer be immersed in the hot water, and also in the cold, previously to the mixture, the instrument should point, after the mixture, to the arithmetical mean, or to half the difference of the separate heats, added to the less, or subtracted from the greater. This will be proved to be actually the fact, by the following experiment:—Mix a pound of water at 172° with a pound at 32°. Half the excess of the caloric of the hot water will pass to the colder portion; that is, the hot water will be cooled 70°, and the cold will receive 70° of temperature; therefore, 172 — 70, or 32 + 70 = 102, will give the heat of the mixture. To attain the arithmetical mean exactly, several precautions must be observed, which have been pointed out in Dr. Crawford's Essay on Heat, p. 95.

The experiments of De Luc, however, have shown that the ratio of expansion does not *strictly* keep pace with the actual increments of temperature; and that the amount of the expansion increases with the temperature. Thus if a given quantity of mercury, in being heated from 32° to 122°, the first half of the scale, be expanded 14 parts, in being raised from 122° to 212°, the higher half, it will be expanded 15 parts.

From the inquiries of Mr. Dalton, it appears to follow, that the irregularity of the expansion of mercury is even considerably greater than has been stated by De Luc. By the common mercurial thermometer we cannot ascertain the true rate of expansion in quicksilver, since the enlarged capacity of the glass ball, in which the fluid is contained, must necessarily affect the result. If the capacity of the ball remained unaltered, we should then be able to determine the actual rate of expansion; but by an increase of temperature its capacity is enlarged, and space is thus found, within the ball, for the expansion of that mercury, which would otherwise be driven into the tube. By knowing the rate of expansion in glass itself, we can correct this error; but a small mistake in this datum will lead us considerably wrong as to the true expansion of quicksilver. The *real* expansion of mercury in glass is *greater* than the *apparent*, by the expansion of the glass itself.

Making due correction for this circumstance, Mr. Dalton was led to conclude, from his experiments, that, notwithstanding the apparent diversities of expansion in different fluids, they all actually expand according to the same law—*viz., that the quantity of expansion is as the square of the temperature from their respective freezing points, or from their points of greatest density.* If then a thermometer were constructed, with degrees corresponding to this law, they would be found to differ very considerably from those of the common mercurial thermometer, in which the space between freezing and boiling is divided into 180 equal parts. But the accuracy of the principle, on which this proposed modification of the thermometric scale is founded, has not been confirmed by subsequent experience.

The view which has been taken by Mr. Dalton of the thermometer has drawn the attention of Dr. Ure,* and of MM. Petit and Dulong,† to the same subject. The former concludes, from his experiments, that taking three thermometric intervals from 32° Fah. upwards, each of 180°, mercury has actually an increasing rate of expansion, and that 60 parts at 572° are expanded as much by the same power of caloric, as 61 parts at 392°, and 62 parts at 212°.

* "Phil. Trans." 1818. † "Annals of Philos.," Vol. XIII.

But this small difference is compensated by the lessening quantity of quicksilver in the bulb of a thermometer at high temperatures, in consequence of which the mercurial thermometer becomes a true measurer of sensible heat. Petit and Dulong, also, satisfied themselves that the expansibility of mercury slowly increases as the temperature augments. From — 40° to 212°, it is scarcely appreciable, and corresponds with the expansion of air, which they take for granted to be perfectly equable. The following table exhibits the dilation of mercury for a degree centigrade at the various temperatures (all centigrade*) indicated in the first column of the table, and measured by an air thermometer :—

Temperature.	Expansion of Mercury.	Temp. indicated by the dilatations of the mercury supposed uniform.
0°	0	0·00
100	$\frac{1}{5550}$	100·00
200	$\frac{1}{5485}$	204·61
300	$\frac{1}{5300}$	314·15

Comparing the numbers in the first and last columns, it appears that up to 100° the mercurial and air thermometers give the same indications; in the second interval, the excess of the former over the latter is 4·61°, and in the last interval it increases to 14·15 centigrade degrees.

More lately the endeavour to reconcile the discrepancy of indications between air thermometers and mercurial ones has been resumed by M. Regnault, the abstract of whose observations on this point are as follows. This philosopher has arrived at the conclusion that the indications of the air thermometer almost exactly accord with those of the mercurial thermometer, between 0° and 100° (centigrade), which pretty nearly accords with the deductions of preceding observers. It is worthy of remark, however, that in M. Regnault's observations, the air thermometer manifests a retardation as compared with the mercurial thermometer, of about 0·2ths of a centigrade degree towards the middle of the scale, a circumstance which seems to indicate that even for this range there is a difference between the expansive progression; the difference, however, is so small, that he believes it need not enter into calculation, more especially as it falls within the limits of uncertainty, dependent on alteration of the zero point in thermometers, on account of slow contraction of their bulbs.

Above 100 degrees centigrade, the mercurial thermometer keeps pace with the air thermometer pretty equally until about 250° C., from which point upwards the mercurial gains on the air thermometer. At 300° C. the difference amounts to 1 degree; at 325° C. it amounts to 1°,75; and at 350° C. the difference is 3 degrees between the indications of the two varieties of thermometers. According to M. Regnault, two air thermometers are always comparable, without reference to the *kind* of glass of which they may be made. This is not the case with mercurial thermometers, which, to be comparable, must be made of the same *kind* of glass; the different rate of expansion between different varieties of which would otherwise introduce an element of great practical discordance. A *tendency* to the same kind of error also exists when air thermometers are the subject of experiment; but in this case the rate of expansion of air

* To convert centigrade degrees into those of Fah., double them, then deduct one-tenth, and add the constant number 32. Thus 18° centigrade × 2 = 36, from which $\frac{1}{10}$ subtracted leaves 32·4, and to this adding 32 we have 64·4 Fah.

so greatly exceeds that of glass, of whatever variety, as to diminish the resulting error to an inappreciable extent, as may be seen by reference to the following table, which shows that the increase of length proportionate to an increase of temperature from 32° to 212° Fah., is for the following substances, as indicated by the accompanying table, and the cubic increase, three times as much :—

Flint glass	$\frac{1}{1316}$ or 0·000022
Crown glass	$\frac{1}{1037}$
Copper	$\frac{1}{588}$
Brass	$\frac{1}{532}$
Soft iron	$\frac{1}{815}$
Steel	$\frac{1}{928}$
Gold	$\frac{1}{681}$
Silver	$\frac{1}{524}$
Lead	$\frac{1}{351}$
Tin	$\frac{1}{468}$

Now the mean cubic expansion for all gases between 32° and 212° Fah. we have already accepted as being ·3665 of their bulk at 32°; hence the ratio of expansive variation of air to flint glass, between the degrees indicated, is as ·3665 to 0·000022, which is altogether unimportant.

These remarks will suffice to show that although thermometers of various kinds,—some of air, some of mercury, some of alcohol,—are used in the course of investigation, yet an accurate means of passing from the range of one kind to the range of another kind is still a desideratum; and the exact rendering of thermal degrees indicated by one kind of thermometer into those of another kind, is a matter of impossibility in the present state of our knowledge. At one time continental philosophers aimed at the employment of air thermometers exclusively, whenever practicable, stimulated by the hope of thereby developing new laws of thermal expansion. For many years the position was admitted, as I have already stated, that all gases expanded equally for equal degrees of temperature. This law created the supposition that the dilatation of gases was proportional to real quantities of heat. At this time, however, when it is known that the coefficient of dilatation is *not* equal for all gases,—that it even varies for the same gas under different pressures,—the air thermometer has lost all theoretical advantages which were conceded to it in consequence of the acceptance of these laws. At present, the only theoretical advantage possessed by it over other thermometers is, that any two instruments of this description are always comparable.

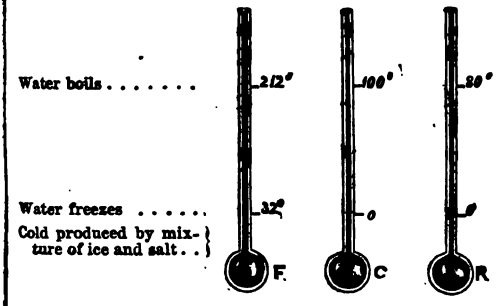
The boiling point of mercury, according to MM. Petit and Dulong, is 680° Fah., or, making the due correction for the expansion of glass, 662° of Fah. scale. The experimental result of Mr. Crighton, of Glasgow, was 656°.

Scales of Thermometric Graduation.—Although all modern thermometers are graduated between two fixed points of temperature—namely, the freezing of water and the boiling of water, under a mean atmospheric pressure of 30° Bar.—nevertheless, the number of degrees into which this space is divided varies. Three principal schemes of graduation present themselves, all of which must be examined, and a rule devised for effecting their mutual conversion.

The three scales are (1) of Fahrenheit, (2) of Celsius, usually termed the Centigrade scale, (3) the scale of Reaumur.

The accompanying diagram will assist the reader in comprehending the difference existing between the three.

From an inspection of this diagram, it will be observed that independently of any variation in the interval between freezing to boiling—a point which will be discussed presently—the scale of Fahrenheit manifests the peculiarity of denominating the freezing point of water as 32°; whereas the scale of Centigrade and of Reaumur represent the same as 0, or zero. The reason why the seemingly irrational number 32° should have been adopted by Fahrenheit as indicative of the freezing point of water, does not appear. Suffice it to remark, that the number was adopted by him in deference to some theoretical speculation.



The further difference existing between the three systems of graduation is as follows:—the Fahrenheit scale establishes 180 divisions between the freezing and the boiling point of water; the scale of Celsius (centigrade) 100; and the scale of Reaumur only 80°. Inasmuch as the freezing point in Fahrenheit's scale is 32°, and there are 180° between 32° and the boiling point of water, it follows that the latter must be 212°, or 32° + 180°. The boiling point, however, according to the Centigrade scale, is necessarily 100°, and of Reaumur necessarily 80°. These data being considered, we can readily convert the degrees of one thermometer into their equivalent degrees of a second. Thus, from the following proportion, it will be observed that a Fahrenheit degree is five-ninths of a Centigrade degree; seeing that *the number of Fahrenheit degrees between the freezing to the boiling point, is to the number of Centigrade degrees for the same space, as unity is to five-ninths.* Thus,

$$\overset{\text{F.}}{(212 - 32) = 180} : \overset{\text{C.}}{100} :: \overset{\text{F.}}{1} : \overset{\text{C.}}{\tfrac{100}{180} = \tfrac{5}{9}}$$

Therefore, to convert Fahrenheit degrees into their equivalents on the Centigrade scale, first subtract 32°, which leaves 180°, then multiply this number by five and divide by nine. Thus we have

$$212 - 32 = \frac{180 \times 5}{9} = \frac{900}{9} = 100.$$

Conversely each Centigrade degree is larger than the corresponding Fahrenheit degree, in the ratio of $\frac{9}{5}$ to 1; hence to reduce Centigrade degrees to those of Fahrenheit, multiply by nine, divide by five, and add thiry-two. For instance, it is required to reduce 100° C. to their Fahrenheit equivalent. Here $\frac{100 \times 9}{5} = 180 + 32 =$ 212° F.; and 212° F., the boiling point of water, we know to be the equivalent of 100° C.

When it is required to convert negative degrees, or degrees below zero (thus — 1° — 2°, &c.), into their corresponding degrees on another scale, precisely the same rule of calculation holds good; although, when stated in common terms, it seems different.

An example will render this plain. It is desired to represent 5° below zero, or — 5° of C., by its equivalent F. 32°, with 9° subtracted, or remainder + 23° is the number.

If the operation be viewed algebraically, the reader will see that the rule of multiplying by nine, dividing by five, and adding thirty-two, has been implicitly followed; only the 5° here being a *negative* quantity (— 5°), it ultimately yields a negative 9° (— 9°), which added to + 32° is equivalent to subtracting a positive 9°. Thus,

$$\frac{-5 \times 9}{5} = \frac{-45}{5} = -9 + 32 = +23.$$

The appended formulæ will perhaps serve to fix the steps of these calculations in the memory.

Fahrenheit to Centigrade, $\frac{F. - 32 \times 5}{9} = C.$

Centigrade to Fahrenheit, $\frac{C. \times 9}{5} + 32 = F.$

Fahrenheit to Reaumur, $\frac{F. - 32 \times 4}{9} = R.$

Reaumur to Fahrenheit, $\frac{R. \times 9}{4} + 32 = F.$

The steps involved in the two last formulæ have not been explained, because it is assumed they are self-evident, $\frac{4}{9}$ expressing the ratio $\frac{80}{180}$, or the ratio of degrees Reaumur to degrees Fahrenheit.

Motion of Free Caloric.—1. Its Radiation. 2. Its Passage through Solids and Fluids.

Caloric Escapes from Bodies in Two Different Modes.—Part of it finds its way through space, independently of other matter, and with immeasurable velocity. In this state it has been called radiant heat, or radiant caloric.

Radiant caloric exhibits several interesting properties.

1. *Its Reflection.* (*a*) Those surfaces that reflect light most perfectly, are not equally adapted to the reflection of caloric. Thus, a glass mirror, which reflects light with great effect when held before a blazing fire, scarcely returns any heat, and the mirror itself becomes warm. On the contrary, a polished plate of tin, or a silver spoon, when similarly placed, reflects, to the hand, a very sensible degree of warmth; and the metal itself remains cool. Metals, therefore, are much better reflectors of caloric than glass; and they possess this property in a higher degree, in proportion to the perfection with which they are polished.

(*b*). Caloric is reflected according to the same law that regulates the reflection of light. This is proved by an interesting experiment of M. Pictet; the means of repeating which may be attained at a moderate expense. Provide two reflectors of planished tin, which may be twelve inches in diameter, and segments of a sphere of nine inches radius. Parabolic mirrors are still better adapted to the purpose; but they are more expensive. Each of these must be furnished, on its convex side, with the means of supporting it in a perpendicular position on a proper stand. Place the mirrors opposite to each other on a table, at a distance of from six to twelve feet. Or they may be placed in a horizontal position, as represented in the wood-cut at page 100, an arrangement in some respects more convenient. In the focus of one, let the ball of an air thermometer, or (which is still better) one of the balls of a differential

thermometer, be situated; and in that of the other, suspend a ball of iron, about four ounces in weight, and heated below ignition, or a small matrass of hot water; having previously interposed a screen before the thermometer. Immediately on withdrawing the screen, the depression of the column of liquid, in the air thermometer, evinces an increase of temperature in the instrument. In this experiment the caloric flows first from the heated ball to the nearest reflector; from this it is transmitted, in parallel rays, to the surface of the second reflector, by which it is collected into a focus on the instrument. This is precisely the course that is followed by radiant light; for, if the flame of a taper be substituted for the iron ball, the image of the candle will appear precisely on that spot (a sheet of paper being presented for its reception) where the rays of caloric were before concentrated.

(*c*). When a glass vessel, filled with ice or snow, is substituted for the heated ball, the course of the coloured liquid in the thermometer will be precisely in the opposite direction; for its ascent will show, that the air in the ball is cooled by this arrangement. This experiment, which appears, at first view, to indicate the reflection of cold, presents, in fact, only the reflection of heat in an opposite direction; the ball of the thermometer being, in this instance, the hotter body. "And since heat emanates from bodies in quantities greater as their temperature is higher, the introduction of a cold body into the focus of one mirror, necessarily diminishes the temperature of a thermometer in the focus of the other, in the same manner as a black body placed in the focus of the one would diminish the quantity of light in the focus of the other."*

(*d*). In Mr. Leslie's "Enquiry into the Nature, &c., of Heat," a variety of important experiments are detailed, which show the influence of covering the reflectors with various substances, or of mechanically changing the nature of their surfaces, on their power of reflecting caloric.

2. Caloric is *refracted*, also, according to the same law that regulates the refraction of light. This interesting discovery we owe to Dr. Herschel, whose experiments and apparatus will be found in the seventh volume of the "Philosophical Magazine."

3. The nature of the *surface* of bodies has an important influence over their power of *radiating* caloric.

To exhibit this influence experimentally, let a canister of planished block tin, forming a cube of six or eight inches, be provided, having an orifice at the middle of its upper side, from half an inch to an inch in diameter, and the same in height. This orifice is intended to receive a cap having a small hole, through which a thermometer is inserted, so that its bulb may reach the centre of the canister. Let one side of the canister be covered with black paint; destroy the polish of another side, by scratching it with sand-paper; tarnish a third with quicksilver; and leave the fourth bright. Then fill the vessel with boiling water. The radiation of caloric from the blackened side is so much more abundant than from the others, as even to be sensible to the hand. Place it before a reflector in lieu of the heated iron ball already described. The thermometer, in the focus of the second reflector, will indicate the highest temperature, or most copious radiation of caloric, when the blackened side is presented to the reflector; less, when the tarnished or scratched side is turned towards it; and least of all, when the polished side.

Mr. Leslie showed, also, the influence of the inclination of a surface, with respect to a given direction of calorific rays, upon the intensity of the effect produced; and

* "Davy's Chem. Philos.," p. 206.

first proved, experimentally, that the action of a radiant surface is proportional to the *sine of the angle formed* by that surface with the direction of the emitted rays.

4. The varieties in the radiating power of different surfaces are attended, as might be expected, with corresponding variations in the *rate of cooling*. If water in a tin vessel, all of whose sides are polished, cools through a given number of degrees in eighty-one minutes, it will descend through the same number in seventy-two minutes, if the surface be tarnished with quicksilver. Water, also, inclosed in a clean and polished tin ball, cools about twice more slowly than water in the same ball covered with oiled paper. Blackening the surface with paint, or even a thin coat of varnish, on the same principle, accelerates greatly the rate of cooling. These facts teach us, that vessels, in which fluids are to be kept long hot, should have their surfaces brightly polished; the best reflectors of heat being the worst radiators. The superiority of metallic tea-pots, for instance, over those of earthenware, depends on the superior polish of their surface; and the manufacturers of earthenware now increase its power of retaining heat by a thin film of some kind of polished metal.

5. Radiant heat has the power of penetrating and passing through transparent bodies, such as plates of glass. The dull heat of a common fire is transmitted, according to Mariotte, with difficulty, and the heat from a matrass of boiling water not at all. De Laroche has shown that the loss of heat, transmitted through glass plates, is less, as the temperature of the source from which it emanates is more elevated. From a body heated to 182°, only $\frac{1}{20}$ of all the heat emitted passed through a glass screen; from one at 340°, $\frac{1}{10}$ of the whole; and from one at 960°, a much larger proportion, *viz.* $\frac{1}{4}$, appeared to pass through the screen. The same philosopher ascertained that the heat which has penetrated through a plate of glass, experiences, in its passage through a second plate, a loss proportionally much smaller in amount. He found, also, that a thick glass screen, though more permeable by light than a thin one of inferior quality, allowed much less radiant heat to pass, and that the difference became smaller as the temperature was raised. In all these cases, it is supposed that the screens are placed at equal distances from the radiating body; for otherwise the effect will be greatly modified by that well established law of radiant heat, according to which its intensity diminishes in proportion to the square of the distance from its source. These facts, some of which had been called in question, have been fully confirmed by Mr. Ritchie.*

6. Radiant caloric is *absorbed* with different facilities by different surfaces. This is only stating, in other terms, that surfaces are endowed with various powers of reflecting caloric; since the power of absorbing caloric is precisely opposite to that of reflecting it. Hence the best reflectors of heat will absorb the least. It may be proper, however, to offer some illustrations of the principle under this form.

(*a*). Expose the bulb of a sensible thermometer to the direct rays of the sun. On a hot summer's day it will probably rise, in this climate, to 108°. Cover it with Indian ink, and again expose it in a similar manner. During the evaporation of the moisture it will fall; but, as soon as the coating becomes dry, it will ascend to 118°, or upwards, of Fahrenheit, or 10° higher than when uncovered with the pigment.† This cannot be explained by supposing that the black coating is gifted with the power of retaining caloric, and preventing its escape; because, from experiments already related, it appears that a similar coating accelerates the cooling of a body to which it is applied.

(*b*). Colour has considerable influence over the absorption of caloric. This is shown by the following very simple experiment of Dr. Franklin.

* "Brewster's Journal," No. xiv. p. 300. † "Watson's Essays," v. 133.

On a winter's day, when the ground is covered with snow, take four pieces of woollen cloth, of equal dimensions, but of different colours, *viz.*, black, blue, brown, and white, and lay them on the surface of the snow, in the immediate neighbourhood of each other. In a few hours, the black cloth will have sunk considerably below the surface; the blue almost as much; the brown evidently less; and the white will remain precisely in the same situation. Thus it appears, that the sun's rays are absorbed by the dark-coloured cloth, and excite such a durable heat, as to melt the snow underneath; but they have not the power of penetrating the white. Hence the preference generally given to dark-coloured clothes during the winter season, and to light-coloured ones in summer, appears to be founded on a sound principle.

(*c*). This experiment has been varied by Sir H. Davy, in a manner which may be repeated at any season of the year. Take six similar pieces of sheet copper, each about an inch square, and colour the one white, another yellow, a third red, the fourth green, the fifth blue, and the sixth black. On the centre of one side of each piece put a small portion of a mixture of oil and wax, or cerate, which melts at about 76°. Then expose their coloured surfaces, under precisely equal circumstances, to the direct rays of the sun. The cerate on the black plate will begin to melt perceptibly before the red; the blue next; then the green and the red; and, lastly, the yellow. The white will scarcely be affected, when the black is in complete fusion.

Solid and Liquid Conductors of Caloric.—Caloric passes, also, but much more slowly, through solid and liquid bodies, which are then termed *conductors* of caloric.

1. Solid bodies convey heat in all directions, upwards, downwards, and laterally; as may be shown by heating the middle of an iron rod, and holding it in different directions. Professor Pictet, indeed, by concentrating the sun's rays upon the middle of a rod of metal, kept in the axis of a glass tube, which was exhausted by the air-pump, found that of two thermometers in contact with the metal, the upper one indicated a quicker elevation of the mercury; but this may be accounted for by the imperfection of the vacuum, and the carrying power of the air unavoidably left in the tube.

2. Some bodies conduct caloric much more quickly than others. Coat two rods, of equal length and thickness, the one of glass, the other of iron, with wax, at one end of each only; and then apply heat to the uncoated ends. The wax will be melted much sooner from the end of the iron rod than from the glass one; which shows, that iron conducts heat more quickly than glass.

Even the different metals possess very different powers of conducting caloric. An approximation to the degree in which they possess this property may be attained by the following method, originally employed by Dr. Ingenhous. Procure several solid cylinders, or rods, of the same size and shape, but of different metals. They may be six inches long, and one-fourth of an inch in diameter. Coat them, within about an inch of one end, with bees-wax, by dipping them into this substance when melted, and allowing the covering to congeal. Let an iron heater be provided, in which small holes have been drilled, that exactly receive the clean ends of the cylinders. After heating it below ignition, insert the cylinders in their places. The conducting power may be estimated by the length of wax coating melted from each in a given time. According to the experiments of Dr. Ingenhous, the metals may be arranged in the following order:—Silver possesses the highest conducting power; next gold; then

copper and tin, which are nearly equal; and, below these, platina, iron, steel, and lead, which are greatly inferior to the rest.

Despretz has recently given the following table:—*

TABLE OF THE COMPARATIVE CONDUCTING POWERS OF THE PRINCIPAL METALS, AND OF SOME EARTHY BODIES.

Gold (greatest conducting power)	1000,0
Silver	973,0
Platinum	981,0
Copper	898,2
Iron	374,3
Zinc	363,0
Tin	303,9
Lead	179,6
Marble	23,6
Porcelain	12,2
Earth of Bricks and Furnaces	11,4

The conducting powers of bodies have been investigated by M. Fourier,† with the aid of an instrument contrived by him for the purpose, to which he has given the name of *Thermometer of Contact*. In its simplest form, it consists of a conical vessel of very thin sheet iron, filled with mercury, closed at its circular base with very thin parchment. A thermometer, whose bulb is plunged into the mercury, indicates, at each instant, the temperature of the liquid mass. By means of the flexible bottom of the cone, exact contact is made with a support placed under it, and kept at a given temperature, such as that of an apartment. When the conducting power of any substance is to be tried, a small circular disc, of the same size as the base of the cone, cut out of the substance to be tried, may be interposed between the flexible bottom and the support. The mercury is first heated to a given temperature (generally to 176° Fah.), and the rates of cooling, during equal intervals, are carefully noted down. If we replace the disc by another of a different material, and again observe the descent of the thermometer in equal times, the rate of cooling will be found to differ materially, however thin the plate which has been interposed; for instance, a piece of the finest paper will occasion a sensible difference. Varying the material of the interposed plates produces very striking varieties in the ratio of cooling, and establishes a great difference of conducting power between calico, linen, flannel, and woollen cloth. The circumstance on which the efficacy of the instrument seems to depend, is the close contact effected by means of the flexible bottom; and the results are obtained with the greatest ease, either by employing thin plates, or by placing the instrument containing the heated mercury on a mass of any substance whose conducting power it is desired to know. In equal intervals of time, for example, not exceeding five minutes, the mercury cools with very different velocities, by placing it first on iron, then on sandstone, then on bricks, and lastly on wood. The effect, it is acknowledged by M. Fourier, is a complicated one, and requires attention to some other circumstances, especially to the specific heat of the body under trial, for which due correction must be made. In another instrument, which he also describes under the name of *Ther-*

* "Ann. de Chim. et de Phys." xxxvi. [illegible].

† "Ann. de Chim. et de Phys." iv. [illegible]; vi. [illegible]; xxvii. [illegible] (also "Pogg." ii. [illegible]); xxviii. [illegible], "Ann. de Chim. et de Phys." xxxvii. [illegible]; "Abstr. Pogg." xiii. [illegible].

moscope of Contact, the specific heats of bodies do not share in the effects; but this instrument, being of a more complicated construction, cannot be understood without reference to the plate.* By the first instrument, however, a great variety of curious facts have been ascertained, which could not have been anticipated *à priori*. M. Fourier finds, for instance, that when several discs of different conducting substances are placed under the cone, the order in which they are arranged causes a material difference in the conducting powers of the aggregates.

It is chiefly owing to the different conducting powers of bodies that they affect us, when we touch them, with different sensations of heat or cold. Thus, if we apply the hand in succession to a number of bodies (as a piece of wood, another of marble, &c.), they appear cold in very different degrees. And as this sensation is occasioned by the passage of caloric out of the hand into the body which it touches, that body will feel the coldest which carries away heat the most quickly; or which, in other words, is the best conductor. For the same reason, of two bodies which are heated to the same degree, and both considerably above the temperature of the hand, the best conductor is the hottest to the touch. Thus the money in our pockets often feels hotter than the clothes which contain it.

Amongst the most recent experiments on the conduction of heat by solids are those of M. Senarmont.† His researches were prosecuted, for the most part, on crystalline bodies, the definite molecular condition of which seemed to promise the discovery of some law. His method consisted in heating a plate of the crystal to be examined in the direction of its crystalline axis, and trace the progress of heat-conduction by observing the melting of wax, with which the sides of the crystalline plate had been previously covered. The following are two general deductions to which the philosopher has arrived:—

1stly. In crystals of the rhombohedral system, and media constituted like them, the conducting power varies in such a manner that, supposing a centre of heat to exist within them, and the medium to be indefinitely extended in all directions, the isothermal surfaces are concentric ellipsoids of revolution round the axis of symmetry, or at least surfaces differing but little therefrom.

2ndly. That in crystals having two optic axes, and media constituted like them, if a centre of heat be assumed to exist within, and the crystal to be indefinitely extended in all directions, the isothermal surfaces will be ellipsoids, with three unequal axes, or curve surfaces, differing but little therefrom.

M. Senarmont did not extend his experiments to crystalline bodies of the tessular system, because of the difficulty of obtaining specimens suitable to his wants. Inasmuch, however, as the forces which determine the shaping these crystals appear to be equal in all directions—a circumstance not only inferred from goniometric measurement, but by the discovery of Mitscherlich, that tessular crystals expand equally by heat in all directions—there is great probability that the isothermal surfaces of such crystals are spherical.

3. Liquid and aëriform bodies convey heat on a different principle from that observed in solids, *viz.*, by an actual change in the situation of their particles. That portion of the fluid which is nearest to the source of heat, is expanded, and becoming specifically lighter, ascends, and is replaced by a colder portion from above. This, in its turn, becomes heated and dilated, and gives way to a second colder portion; and thus the process goes on, as long as the fluid is capable of imbibing heat.

* See "Ann. de Chim. et de Phys." xxxvii. 291. † "N. Ann. Chim. Phys." xxi. 457.

(*a*). Take a glass tube, eight or ten inches long, and about an inch in diameter. Pour into the bottom part, for about the depth of an inch, a little water tinged with litmus, and then fill up the tube with common water, pouring on the latter extremely gently, so as to keep the two strata quite distinct. If the upper part of the tube be first heated, the coloured liquor will remain at the bottom; but if the tube be afterwards heated at the bottom, the infusion will ascend, and will tinge the whole mass of fluid.

(*b*). Into a cylindrical glass jar, four inches diameter, and 12 or 14 deep, let a circular piece of ice be fitted 3½ inches thick, and of rather less diameter than the jar. Or water may be poured into the jar to the depth of 3½ inches, and allowed to congeal by exposure to a freezing atmosphere, or by surrounding it with a mixture of snow and salt. The ice is to be secured in its place by two slips of wood, crossing each other like two diameters of a circle, set at right angles to each other. Pour, over the cake of ice, water of 32° temperature, to the depth of two inches; and on its surface let there float a shallow circular wooden box, perforated with holes. From the cock of a tea-urn, filled with boiling water, and raised so that its spout may be above the top of the jar, suspend a number of moistened threads, the lower ends of which must rest on the surface of the box. By this arrangement, when the cock is turned, the hot water will trickle down the threads, and will have its fall considerably broken. It will then spread over the surface of the box, and pass through the perforated holes to the cold water beneath, over which it will float without mixing with it. Let the jar be thus completely filled with hot water. The ice will remain unmelted for several hours at the bottom of the vessel.

(*c*). Fill a similar jar with hot water; and, having provided a cake of ice, of equal size with the former one, let it be placed on the surface of the water. In about three minutes the whole will be melted. Both these experiments are more striking if the water, used for forming the cakes of ice, be previously coloured with litmus; for, in the latter experiment, the descending currents of cold water are thus made strikingly apparent.

(*d*). These experiments may be varied, by freezing, in the bottom of a tube one inch wide, a portion of water, about two inches in depth. Then fill the tube with water of the common temperature, and hold it inclined over an Argand's lamp, so that the upper portion only of the tube may be heated. When thus disposed, the water may be made to boil violently at the surface, and yet the ice will not be melted. But if the experiment be reversed, and (the ice floating on the surface) heat be applied to the bottom of the tube, the ice will be liquefied in a few seconds.

(*e*). Substituting water of the temperature of 41° for the boiling water used in experiment (*c*), Count Rumford found, that, in a given time, a much greater quantity of ice was melted by the cooler water. This appears, on first view, rather paradoxical. The fact, however, is explained by a remarkable property of water, viz., that when cooled below 40° it ceases to contract, and experiences, on the contrary, an enlargement of bulk. Water, therefore, at 40° (at the bottom of which is a mass of ice at 32°), is cooled by contact with the ice, and is expanded at the same moment. It therefore ascends, and is replaced by a heavier and warmer portion from above.

It is in consequence of the same property that the surface of a deep lake is sometimes covered over with ice, even when the water below is only cooled to 40°; for the superficial water is specifically lighter than the warmer water beneath it, and retains its place, till it is changed into ice. This property of water is one of the most remark-

able exceptions to the law, that bodies are expanded by an increase, and contracted by a diminution, of temperature.

From these facts, Count Rumford concluded, that water is a perfect non-conductor of caloric, and that it propagates caloric in one direction only, *viz.*, upwards, in consequence of the motions which it occasions among the particles of the fluid.

The Count inferred also, that if these motions could be suspended, caloric would cease to pass through water; and, with the view of deciding this question, he made the following experiments, which admit of being easily repeated.* A cylindrical tin vessel must previously be provided, two inches in diameter, and 2½ inches deep, having a moveable cover, perforated with a small aperture, for transmitting the stem of a thermometer, which is to be inserted so that its bulb may occupy the centre of the vessel.

(*f*). Fill this vessel with water of the temperature of the atmosphere; let the cover be put in its place; and let the whole apparatus, except the scale of the thermometer, be immersed in water, which is to be kept boiling over a lamp. Observe how long a time is required to raise the water from its temperature at the outset to 180°, and remove it from its situation. Note, also, how long it takes to return to its former temperature.

(*g*). Repeat the experiment, having previously dissolved in the water 200 grains of common starch. The thermometer will now require about half as long again to arrive at the same temperature. A similar retardation, and to a greater amount, is produced by the mixture of fur, eider-down, cotton-wool, and various other substances, which are not chemically soluble in water, and which can diminish its conducting power in no other way than by obstructing the motion of its particles. The same substances retard the propagation of heat through air also, by preventing the movement of its particles among each other. In general, the lighter the non-conductor, as to weight, the better does it act as an envelope to retain heat, and hence the better is it adapted to the purpose of winter clothing. Air thus confined in small cells, appears to be a very slow conductor of caloric.

The inference, however, respecting the complete non-conducting power of water, has been set aside by the subsequent inquiries of Dr. Thomson† and the late Dr. John Murray,‡ of Edinburgh, especially by a most decisive experiment of the latter. To establish the conducting power of water, it was justly deemed indispensable, that caloric should be proved to be propagated through that fluid downwards. This, on actual trial, it appeared to be; but it was objected, that the sides of the containing vessel might be the conductor. To obviate this objection, Dr. Murray contrived to congeal water into the form of a jar, capable of holding liquids. This was separately filled with linseed oil and with mercury. At a proper distance below the surface, the bulb of a thermometer was placed; and on the surface of the liquid rested a flat iron vessel, containing boiling water. Under these circumstances, the thermometer invariably rose; and though it ascended only a very few degrees, yet it must be recollected, that the cooling power of the sides of the vessel would effectually prevent any considerable elevation of temperature. This experiment, in conjunction with others, decisively proves that water is a conductor, though a slow or imperfect one, of caloric.

* See his "Seventh Essay on Heat," 8vo, 1797.

† Nicholson's "Phil. Journ.," vol. iv. p. 529.

‡ Ibid, vol. i., pp. 165 and 241.

Caloric the Cause of Liquidity.—Almost every solid is capable of passing to the fluid state on the application of a sufficient degree of heat, which is not the same for all solids, but differs for each. In many solids the transition to the liquid form is sudden, while others pass through various stages of liquidity before they become completely fluid. The metals and ice are examples of the first, and wax or tallow of the second, kind of liquefaction. In the former, it is more easy to determine what has been called the *fusing* or *melting point*, which is constant in the same solid.

All fluids, with the exception of chloride of azote, protochloride of carbon, sulphuret of carbon, and alcohol, are capable of being solidified by reducing their temperature. When the natural form of a body is that of a liquid, and it only occasionally assumes the solid form, we call the temperature at which it is solidified, or at which, when solid, it begins to melt, the *freezing* or *congealing point;* and this is also constant in the same liquid, but different in various liquids, as will more clearly appear from the following examples.

I. *The temperature of melting snow, or of thawing ice, is uniformly the same at all times, and in all places.*—This may be ascertained by the thermometer, which will always, when immersed in liquefying ice or snow, point to 32° Fah., whatsoever may be the height of the barometer, or the elevation, above the sea, of the place where the experiment is made.*

II. *The sensible heat or temperature of ice, of* 32° *Fah., is not changed by liquefaction.*—A thermometer in pounded ice stands at 32°, and at the very same point in the water which results from the liquefaction of ice: care being, of course, taken to observe the temperature of the water, at the moment when the last portion of ice has been liquefied.

III. *Yet ice, during liquefaction, must absorb much caloric.*—Expose a pound of water at 32°, and a pound of ice at 32°, in a room, the temperature of which is several degrees above the freezing point, and uniformly the same during the experiment. The water will arrive at the temperature of the room several hours before the ice is melted; and the ice, when first melted, will exhibit, as before its liquefaction, the temperature of 32°. Yet the ice, during the whole of this time, must have been imbibing caloric, because a colder body can never be in contact with a warmer one without receiving caloric from it. The caloric, therefore, which has entered the ice, but is not to be found in it by the thermometer, is said to have *become latent*. As it is the cause of the liquefaction of the ice, it is sometimes called *caloric of fluidity*, or *constituent caloric*.

IV. *The quantity of caloric that enters into a pound of ice, and becomes latent, during liquefaction, may be learned by experiment.*—To a pound of water, at 172°, add a pound of ice at 32°. The temperature will not be the arithmetical mean (102°), but much below it—viz., 32°. All the excess of caloric in the hot water has therefore disappeared. From 172° take 32°; the remainder, 140°, shows the quantity of caloric that enters into a pound of ice during liquefaction; that is, as much caloric is absorbed by a pound of ice, during its conversion into water, as would raise a pound of water from 32° to 172°.

It is from the property of its uniformly absorbing the same quantity of caloric for conversion into water, that ice was applied, by Lavoisier and Laplace, to the admeasurement of the heat evolved in certain operations. Let us suppose the body (from which the caloric, evolved either by simple cooling or combustion, is to be measured)

* Shuckburgh, "Philosophical Transactions," lxix.

to be inclosed in a hollow sphere of ice, with an opening at the bottom. When thus placed, the heat which is given out will be all employed in melting the ice; and will produce liquefaction in direct proportion to the quantity of heat evolved. Hence the quantity of ice which is converted into water will be a measure of the caloric that is separated from the body submitted to experiment. In this way, Lavoisier ascertained that equal weights of different combustible bodies melt, by burning, very different weights of ice. The apparatus which he employed for this purpose he has called the *calorimetèr*. Its construction can scarcely be understood without the plate, which accompanies the description in his "Elements of Chemistry;" and I consider it unnecessary to copy it into this work, because the instrument is liable to several causes of fallacy, which render it quite inadequate to the accurate measurement of heat.

V. *The heat rendered latent by the fusion of various bodies is not a constant quantity, but various for each individual body.*—This is shown by the following results of the experiments of the two Drs. Irvine:—

	Caloric of fluidity.	Do. reduced to the sp. heat of water.
Sulphur	143·68° Fah.	27·14
Spermaceti	145	
Lead	162	5·6
Bees-wax	175	
Zinc	493	48·3
Tin	500	33·
Bismuth	550	23·25

All the bodies enumerated in the table require, it may be observed, more caloric to bring them into a fluid state than is necessary to convert ice into water, for which 140° are sufficient.

VI. *Other examples of the absorption of caloric, during the liquefaction of bodies*, are furnished by the mixture of snow and nitric acid, or of snow and common salt, both of which, in common language, produce intense cold.

1. Dilute a portion of nitric acid with an equal weight of water; and when the mixture has cooled, add to it a quantity of light fresh-fallen snow. On immersing the thermometer in the mixture, a very considerable reduction of temperature will be observed. This is owing to the absorption and intimate fixation of the free caloric of the mixture by the liquefying snow.

2. Mix quickly together equal weights of fresh-fallen snow at 32°, and of common salt, cooled, by exposure to a freezing atmosphere, down to 32°. The two solid bodies, on admixture, will rapidly liquefy, and the thermometer will sink 32°, or to 0; or, according to Sir C. Blagden, to 4° lower.* To understand this experiment, it must be recollected that the snow and salt, though at the freezing temperature of water, have each a considerable portion of uncombined caloric. Now salt has a strong affinity for water; but the union cannot take place while the water continues solid. In order, therefore, to act on the salt, the snow absorbs all the free caloric required for its liquefaction; and, during this change, the free caloric, both of the snow and of the salt, amounting to 32°, becomes latent, and is concealed in the solution. This solution

* "Philosophical Transactions," lxxviii. 281.

remains in a liquid state at 0, or 4° below 0 of Fah.; but, if a greater degree of cold be applied to it, the salt separates in a concrete form.

3. Most neutral salts, also, during solution in water, absorb much caloric; and the cold thus generated is so intense as to freeze water, and even to congeal mercury. The former experiment, however (*viz.*, the congelation of water), may easily be repeated on a summer's day. Add to 32 drachms of water 11 drachms of muriate of ammonia, 10 of nitrate of potassa, and 16 of sulphate of soda, all finely powdered. The salts may be dissolved separately in the order set down. A thermometer, put into the solution, will show that the cold produced is at or below freezing; and a little water, in a thin glass tube, being immersed in the solution, will be frozen in a few minutes.

4. Crystallized hydrochlorate of lime, when mixed with snow, produces a most intense degree of cold. This property was discovered some years ago, by M. Lovitz, of St. Petersburg, and has since been applied, in this country, to the congelation of mercury on a very extensive scale. The proportions which answer best are about equal weights of the salt, finely powdered, and of fresh-fallen and light snow. On mixing these together, and immersing a thermometer in the mixture, the mercury sinks with great rapidity.

For measuring exactly the cold produced, a spirit thermometer, graduated to 50° below 0 of Fah., or still lower, should be employed. A few pounds of the salt are sufficient to congeal a large mass of mercury. By means of 13 pounds of the hydrochlorate, and an equal weight of snow, Messrs. Pepys and Allen froze 56 pounds of quicksilver into a solid mass. The mixture of the whole quantity of salt and snow, however, was not made at once, but part was expended in cooling the materials themselves.

On a small scale, it may be sufficient to employ two or three pounds of the salt. Let a few ounces of mercury, in a very thin glass retort, be immersed, first in a mixture of one pound of each, and, when this has ceased to act, let another similar mixture be prepared. The second will never fail to congeal the quicksilver. The salt thus expended may be again evaporated, and crystallized for future experiments.

VII. *On the contrary, liquids, in becoming solid, evolve or give out caloric, or, in common language, produce heat.*

1. Water, if covered with a thin stratum of oil, and kept perfectly free from agitation, may be cooled down more than twenty degrees below 32°; but, on shaking it, or dropping into it a small fragment of ice, it immediately congeals, and the temperature rises to 32°.*

2. Expose to the atmosphere, when at a temperature below freezing (for example, at 25° of Fahrenheit), two equal quantities of water, in one only of which about a fourth of its weight of common salt has been dissolved. The saline solution will be gradually cooled, without freezing, to 4°. The pure water will progressively descend to 32°, and will there remain stationary a considerable time before it congeals. Yet, while thus stationary, it cannot be doubted that the pure water is yielding caloric to the atmosphere equally with the saline solution; for it is impossible that a warmer body can be surrounded by a cooler one without imparting caloric to the latter. The reason of this equable temperature is well explained by Dr. Crawford. Water, he

* Blagden, "Philosophical Transactions," 1788.

observes, during freezing, is acted upon by two opposite powers: it is deprived of caloric by exposure to a medium whose temperature is below 32°; and it is supplied with caloric by the evolution of that principle from itself, *viz.*, of that portion which constituted its fluidity. As these powers are exactly equal, the temperature of the water must remain unchanged till the caloric of fluidity is all evolved.

3. The evolution of caloric, during the congelation of water, is well illustrated by the following experiment of Dr. Crawford:—Into a round tin vessel put a pound of powdered ice; surround this by a mixture of snow and salt in a larger vessel; and stir the ice in the inner one till its temperature is reduced to + 4° of Fahrenheit. To the ice thus cooled, add a pound of water at 32°. One fifth of this will be frozen; and the temperature of the ice will rise from 4° to 32°. In this instance the caloric, evolved by the congelation of one fifth of a pound of water, raises the temperature of a pound of ice 28°.

4. If we dissolve sulphate of soda in water, in the proportion of one part to five, and surround the solution by a freezing mixture, it cools gradually down to 31°. The salt at this point begins to be deposited, and stops the cooling entirely. This evolution of caloric, during the separation of a salt, is exactly the reverse of what happens during its solution.*

5. To a saturated solution of sulphate of potassa in water, or of any salt that is insoluble in alcohol, add an equal measure of alcohol. The alcohol, attracting the water more strongly than the salt, precipitates the salt, and considerable heat is produced.

Caloric the Cause of Vapour.—I. *Every liquid, when of the same degree of chemical purity, and under equal circumstances of atmospheric pressure, has one peculiar point of temperature at which it invariably boils.*—Thus pure water always boils at 212°, alcohol of sp. gr. 0·813 at 173°, and ether at 96° Fah.; and, when once brought to the boiling point, no liquid can be made hotter, however long the application of heat be continued.

The boiling point of water may be readily ascertained by immersing a thermometer in water boiling, in a metallic vessel, over the fire. As there is some danger in applying heat directly to a vessel containing either ether or alcohol, the ebullition of these fluids may best be shown by immersing the vessel containing them in water, the temperature of which may be gradually raised. The appearance of boiling is owing to the formation of vapour at the bottom of the vessel, and its escape through the heated fluid above it. That the steam which escapes is actually formed at the bottom, and not at the top of the water, may be seen by boiling some water in a Florence flask, or other transparent vessel, over an Argand's lamp. The bubbles of vapour will evidently ascend from the bottom of the vessel.

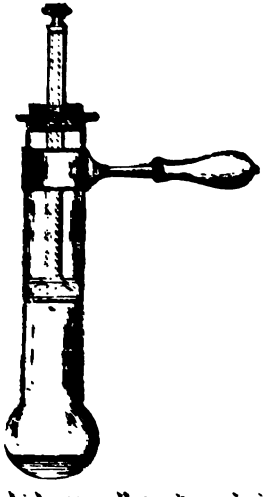
A few exceptions to the fixity of the boiling point of liquids, arising chiefly from the material of which the containing vessel is made, have been stated by Gay Lussac.† Under a mean pressure, the boiling point of water in a metallic vessel is generally 212°; in a glass vessel it rises as high as 216°, but may be stated, on an average, at 214°. Even in the same glass vessel the boiling point is found to vary considerably. This appears to be owing to some irregularity in the formation of steam, which may be observed to burst forth occasionally in large bubbles, the escape of which is immediately followed by a fall of the thermometer. If iron or copper filings, platinum wire, or even

* Blagden, "Philosophical Transactions," lxxviii. 290.

† "Ann. de Chim. et de Phys." vii. 307, or "Journ. of Science," v. 361.

pounded glass, be thrown into the glass vessel of water thus heated, steam is instantly formed in great abundance, and the boiling point is immediately lowered two or three degrees. By putting coils of wire into liquids, heated in glass vessels with a view to their distillation, they are made to boil quietly, and some degrees lower than they would otherwise do. It is, of course, necessary to use a metal which is not acted upon by the particular fluid under distillation—platinum, for instance, when we operate on sulphuric acid. A similar change of the boiling point, by the presence of extraneous substances, has been found by Dr. Bostock to take place in ether and alcohol. Ether, heated in a glass vessel, had its boiling point lowered nearly 50° by introducing a few chips from a cedar pencil, and alcohol of s. g. ·849 had its boiling point reduced by the same means, between 30° and 40°. The boiling point of water, heated in a glass vessel, was brought down 4° or 5° by the same method.*

II. *Steam has exactly the same temperature as boiling water.*—Let a tin vessel be provided, having two holes in its cover, one of which is just large enough to admit the stem of a thermometer. Fill it partly with water, and let the bulb of the thermometer be an inch or two above the surface of the water, leaving the other aperture open for the escape of vapour. When the water boils, the thermometer, surrounded by steam, will rise to 212°, which is precisely the temperature of the water beneath; yet water, placed on a fire, continues to receive heat very abundantly, even when boiling hot; and as this heat is not appreciable by the thermometer, it must exist in the steam in a latent state. With saline solutions, the temperature of the steam arising from them is the same as that of the boiling solution itself.† The boiling points of a considerable number of saturated solutions are exhibited in the form of a Table in the "Quarterly Journal of Science," xviii. 89.



III. *Perfectly formed steam is completely invisible.*—We may satisfy ourselves of this by boiling strongly a small quantity of water in a flask; for perfect transparency will exist in the upper part of the vessel. It is only when it begins to be condensed that steam becomes visible. We have a proof, also, of the same fact in the thick fogs, which are produced by a sudden transition from warm to cold weather; the vapour, which was imperceptible at the high temperature, being condensed and rendered visible by the lower.

The perfect transparency of steam, and also two other important properties on which depends its use as a moving power, viz., its elasticity and its condensibility by a reduced temperature, are beautifully shown by a little apparatus contrived by Dr. Wollaston, of which a sketch is annexed. It consists of a glass tube about six inches long and three-fourth inch bore, as cylindrical as possible, and blown out a little at the lower end. It has a wooden handle, to which is attached a brass clip embracing the tube; and within is a piston, which, as well as its rod, is perforated, as shown by the dotted lines. This canal may be occasionally opened or closed by a screw at the top; and the piston rod is kept in the axis of the cylinder by being passed through a hole

* "Ann. of Phil." N. S. iii. 186. † "Ann. of Phil." N. S. v. 73.

in a piece of cork fixed at the top of the tube. When the instrument is used, a little water is put into the bottom; the piston is then introduced, with its aperture left open; and the water is heated over a spirit lamp. The common air is thus expelled from the tube, and when this may be supposed to be effected, the aperture in the rod is closed by the screw. On applying heat, steam is produced, which drives the piston upwards. On immersing the bulb in water, or allowing it to cool spontaneously, a vacuum is produced in the tube, and the piston is forced downwards by the weight of the atmosphere. These appearances may be alternately produced, by repeatedly heating and cooling the water in the ball of the instrument. In the original steam engine, the vapour was condensed in the cylinder, as it is in the glass tube; but in the engine as improved by Mr. Watt, the steam is pumped into a separate vessel, and there condensed; by which the loss of heat, occasioned by cooling the cylinder every time, is avoided.

IV. *The boiling point of the same fluid varies under different degrees of atmospheric pressure.*—Thus water, which has been removed from the fire, and has ceased to boil, has its ebullition renewed when it is placed under a receiver, the air of which is quickly exhausted by an air pump. Alcohol and ether, confined under an exhausted receiver, boil violently at the temperature of the atmosphere. In general, liquids boil *in vacuo*, with about 124° less of heat than are required under a mean pressure of the atmosphere;* water, therefore, in a vacuum must boil at 88°, and alcohol at 49° Fah. Even the ordinary variations in the weight of the air, as measured by the barometer, are sufficient to make a difference in the boiling point of water of several degrees between the two extremes,† as shown in the following table:—

Height of Barometer.	Boiling point of water.	Height of Barometer.	Boiling point of water.
26	204·91°	29	210·19°
26·5	205·79°	29·5	211·07°
27	206·67°	30	212°
27·5	207·55°	30·5	212·88°
28	208·43°	31	213·76°
28·5	209·31°		

On ascending considerable heights, as to the tops of mountains, the boiling point of water gradually falls on the scale of the thermometer. Thus, on the summit of Mont Blanc, water was found by Saussure to boil at 187° Fah. On this fact is founded the use of the thermometer in the measurement of heights, which, though originally suggested by Fahrenheit, has only within the last few years been made conveniently practicable, by the invention of a thermometer, adapted to the purpose, by the Rev. Mr. Wollaston.‡ Without entering into minute details, it would not be possible to give a clear idea of the instrument. It may be sufficient to state, that each degree about the boiling point is made to occupy a space that admits of being distinctly divided into 1000 parts. And as each degree of Fahrenheit is equivalent to 0·589 of an inch of the barometer, which indicates an elevation of 530 feet, it follows that one thousandth part of a degree will be equivalent to a difference in height of about six inches. In fact, the height of a common table produces a manifest difference in the boiling point of water, as ascertained by this very sensible instrument.

* Black's Lectures, i. 151.
† Sir G. Shuckburgh, in "Philosophical Transactions," lxxix. 375; and Gen. Roy in ditto, lxvii. 687.
‡ "Philosophical Transactions," 1817.

The influence of a diminished pressure, in causing ebullition to take place at a lower temperature, may also be illustrated by the following simple experiment:—Place over a lamp a Florence flask, about three-fourths filled with water; let it boil briskly during a few minutes; and, immediately on removing it from the lamp, cork it tightly, and suddenly invert it. The water will now cease to boil; but, on cooling the convex part of the flask by a stream of cold water, the boiling will be renewed. Applying boiling water from the spout of a tea-kettle to the same part of the flask, the water will again cease to boil. This renewal of the ebullition, by the application of cold (as apparent paradox), is owing to the formation of an imperfect vacuum over the hot water, by the condensation of steam; and the suspension of boiling, on re-applying the heat, to the renewed pressure on the surface of the hot water, occasioned by the formation of fresh steam.

From the facts which have been stated, it may be inferred that the particles of caloric are mutually repulsive, and that they communicate this repulsive tendency to other bodies in which caloric is contained. This repulsive power tends to change solids into fluids, and liquids into aëriform bodies, and is chiefly counteracted by the pressure of the atmosphere. Were this counteracting cause removed, many bodies, which at present have a liquid form, would cease to be such, and would exist permanently in a gaseous state. Precisely the same effect, therefore, results from the prevalence of either of these forces. Add to certain liquids a quantity of caloric, in other words, place them in a high temperature, and they immediately assume an aëriform state. Again, their temperature remaining the same, diminish the weight of the atmosphere; and the caloric, which they naturally contain, exerts its repulsive tendency with equal effect, and they are in like manner converted into gases. These facts are best shown by the following experiments on ether:—

1. Ether, at the temperature of 96°, exists in the state of a gas. This may be shown by filling a jar with water a few degrees above this temperature, and inverting it in a vessel of the same. Then introduce a little ether, by means of a small glass tube closed at one end. The ether will rise to the top of the jar, and, in its ascent, will be changed into gas, filling the whole jar with a transparent, invisible, elastic fluid. On permitting the water to cool, the ethereal gas is condensed, and the inverted jar again becomes filled with water.

2. Ether is changed into gas by diminishing the weight of the atmosphere. Into a glass tube, about six inches long, and half an inch in diameter, put a tea-spoonful of ether, and fill up the tube with water; then, pressing the thumb on the open end of the tube, place it, inverted, in a jar of water. Let the whole be set under the receiver of an air-pump, and the air exhausted. The ether will be changed into gas, which will expel the water entirely from the tube. On re-admitting the air into the receiver, the gas is again condensed into a liquid.

It is evidently unnecessary that a liquid should boil *in vacuo*, in order to be converted into vapour; for all liquids have, in fact, at every temperature, a tendency to assume the state of gas, and several which exhibit, at the common temperature of the atmosphere, no appearance of ebullition, are nevertheless convertible into vapour, at that temperature, under an exhausted receiver. The quantity of vapour, produced *in vacuo*, varies with the space, the temperature, and the nature of the liquid. 1stly, It is proportional to the space, for a double space gives occasion to the formation of a double quantity of vapour; and if a given volume of vapour be mechanically compressed into half its bulk, one half will be re-converted into water. 2ndly, It increases with the

temperature, but in a greater proportion. 3rdly, It is different for different liquids; and it may be observed that liquids which enter most easily into ebullition are generally, though with some exceptions, those which, at a given temperature, afford the densest vapour. Thus the vapour of ether is more dense than that of water. The caloric required to produce this sort of evaporation, which may be called *spontaneous*, in order to distinguish it from that produced by obvious sources of heat, is supplied in the first instance by the liquid itself, the temperature of which is at first observed to fall, and is afterwards restored by the influx of heat from surrounding bodies.

Spontaneous evaporation goes on, also, from the surface of liquids exposed to the atmosphere, and a quantity of vapour is produced which, from the same liquid, is determined by the pressure and the temperature. If to a given volume of dry atmospheric air, confined over mercury, we admit a small quantity of water, the volume of the air is increased by the admixture of aqueous vapour. Substituting, at the same temperature and pressure, any other gas for atmospheric air, an expansion is produced to precisely the same amount; and it is remarkable that the quantity and force of vapour, in a given volume of air or of gas of extreme moisture, is precisely the same as in a Torricellian vacuum of like volume.* These facts show, as will afterwards more fully appear, that spontaneous evaporation is entirely independent of any affinity of air for water, and is to be explained entirely by the general laws regulating the production and force of vapour.

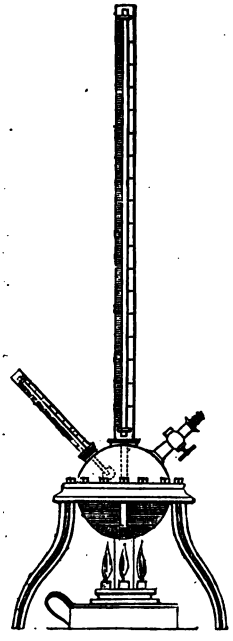
V. *By considerably increasing the pressure, water may be heated to above* 400° *Fah. without being changed into vapour.*—This experiment requires, for its performance, *Papin's digester*, which is merely a strong vessel of iron, or any other tenacious metal, the lid of which is firmly screwed down, after introducing the fluid which is to be heated. To prevent the vessel from being burst, its lid is provided with a safety valve, which may be loaded with any weight that may be thought necessary and prudent. That the boiling point of water, and the temperature of steam, are raised by an increased pressure, may be equally well shown by means of the small boiler, represented at page 153, which will be found extremely useful in experiments on this subject.

On the cock *c* may be screwed, occasionally, a valve, loaded in the proportion of 14 pounds to the square inch; or a gauge adapted to show the density of the steam, by the diminution of volume in a confined portion of air, which will occupy a bulk inversely proportionate to the compressing force (see Fig. p. 153, *f*.) The boiler being rather more than half filled with water, and the perforated cap, *d*, being screwed into its place, the ball of the thermometer will be an inch or more above the surface of the water, and will indicate its temperature, as well as that of the steam, both being, necessarily, in all cases, precisely the same. Allowing the steam to escape through the cock *c*, before affixing the valve, the temperature of the steam, under a mean atmospheric pressure, will be 212°. When an additional atmosphere is added by the weighted valve, it will rise to 250°; by a valve twice as heavy as the first, or loaded in the proportion of 42 pounds to the square inch (= three atmospheres), the temperature of the steam will be raised to more than 270°. This is as far as it is safe to carry the experiment.

An apparatus adapted to the same purposes has been contrived, also, by Dr. Marcet, and may be procured from the makers of philosophical instruments in London. It consists of two hemispheres (see the figure), generally of brass, which are fixed together

* "Dalton's New System," p. 153.

by flanches and screws.



At the upper part are three openings, into one of which a cock may be screwed; into the other a thermometer, graduated to 250°, or upwards; and into the central one is fixed a long glass tube, open at both ends, and reaching to within about one-eighth of an inch of the bottom of the boiler. When the apparatus is used, mercury sufficient to fill the tube is first put into the vessel, and over this a quantity of water sufficient to occupy about half its capacity is poured, and the cock being shut, the heat of a spirit lamp, with three or four wicks, is applied. With this boiler, precisely the same experiments may be made as with that which I have already described, the only difference being in its form, and in the gauge for measuring the force of the steam which is generated; for this, by its pressure, drives the mercury up the tube, and by the height of the column exhibits in a more striking manner the correspondence between the elasticity of the steam and its temperature.

The elasticity of the vapour of water from 32° to 212° Fah. had been experimentally determined by Mr. Dalton, who, from his results, had calculated its force at temperatures above the ordinary boiling point. It was still, however, desirable to ascertain, by actual experiment, the elastic force of vapour above 212°, and this has been attempted by Professor Robinson, Mr. Southern, and Dr. Ure. Mr. Southern's experiments were made many years ago, but were first published in Dr. Brewster's edition of Professor Robinson's works. The following table expresses the elasticity of aqueous vapour according to his experiments, under one, two, four, and eight atmospheres:—

Atmospheres.	Pressure in inches of Mercury.	Temperatures Fah.
1	29·8	212·°
1½	44·7	234·
2	59·6	250·3
2½	74·5	264·2
3	89·4	275·
3½	104·3	285·3
4	119·2	293·4
4½	134·1	302·
5	149·	309·2
5½	163·9	316·4
6	178·8	322·7
6½	193·7	328·5
7	208·6	334·4
7½	223·5	339·3
8	238·4	343·6

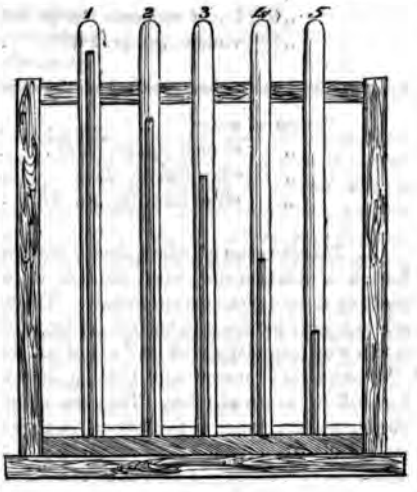
Dr. Ure's experiments were published in the "Philosophical Transactions" for

1818. By reference to his results, it will be seen that between 32° and 212°, an almost exact coincidence may be observed between the experiments of Dalton and of Ure; but this ceases above the boiling point of water, for there Mr. Dalton's numbers were calculated on the presumption that the same law of progression obtains in the higher as in the lower ranges, which does not appear to be correctly the fact.

Dr. Ure has examined, also, the elastic forces of the vapours of alcohol, ether, oil of turpentine, and naphtha, and has exhibited the results in the form of a table. To the experiments on ether it has, however, been objected by Mr. Dalton that they were made on that fluid in an impure state, as is evident from its boiling point, which Dr. Ure states at 104° or 105°; whereas the point at which pure ether boils, under the pressure of the atmosphere, is 96° Fah. Mr. Dalton has, therefore, from his own experiments, constructed a fresh table.

VI. *The density of steam is nearly, if not accurately, proportional to its elasticity;* at least this may be affirmed of it within the limits of Mr. Southern's experiments, which extended to steam formed under a pressure of 120 inches of mercury, or of four atmospheres. Thus steam of elasticity = 40 inches of mercury required 1·430 cubic inches of water to form each cubic foot of steam; vapour of 80 inches required 2·940 cubic inches of water; and vapour = 120 inches force required for each cubic foot 4·279 cubic inches of water. The elasticities, therefore, and the quantities of water in these experiments, have the same common multiple: in other words, steam of double, triple, &c., elastic force contains, in an equal volume, twice, thrice, &c., the weight of water.

VII. *The force of vapour from different liquids varies at the same temperature.*—This is best shown by the following elegant contrivance of Mr. Dalton:—Take a barometer tube, perfectly dry, and fill it with mercury just boiled, marking the place where it is stationary; then, having graduated the tube into inches and tenths, pour a little ether, water, or any other liquid the subject of experiment, into it, so as to moisten the whole inside. After this, again pour in mercury, and invert the tube, carefully excluding air. The barometer, by standing some time, will exhibit a portion of the liquid employed, of one-eighth or one-tenth of an inch, upon the top of the mercurial column, because, being lighter, it ascends by the side of the tube, which may now be inclined, and the mercury will rise to the top, manifesting a perfect vacuum from air. When the ordinary barometer is at the mean height (29·8), and the thermometer at 50°, the force of vapour in the ether barometer will depress the mercury nearly 10 inches; of sulphuret of carbon about 8½ inches; that of alcohol about an inch; and that of water only about



0·4 inch, showing that the force of vapour from each liquid in a vacuum is proportionate to its evaporability.

Exposing vapour thus confined to higher and lower temperatures than that of the atmosphere, Mr. Dalton determined *that the variation of the force of vapour from all liquids is the same for the same variation of temperature, reckoning from vapour of any given force.* Thus, assuming a force equal to 30 inches of mercury as the standard—that being the force of any liquid boiling in the open air—we find aqueous vapour loses half its force by a diminution of 30° of temperature. So, also, does the vapour of any other liquid lose half its force by diminishing its temperature 30° below that at which it boils, and the like for any other increment or decrement of heat. This position Mr. Dalton established by a train of satisfactory experiments.

VIII. *The latent heat of the vapours of fluids, though constant for vapour of the same kind, and of a given elasticity, differs in different vapours.*

The latent heat of the vapours of different liquids has been investigated by Dr. Ure and by M. Despretz. The method employed by both was to distil off a known quantity of each liquid, and to observe the temperature gained by the water employed to condense its vapour. From the results, Dr. Ure has constructed the following table* :—

GENERAL TABLE OF LATENT HEAT OF VAPOURS.

Vapour of water at its boiling point		1000
,,	alcohol (sp. gr. 0·825)	457
,,	sulph. ether (boiling point 104°)	312·9
,,	petroleum	183·2
,,	oil of turpentine (do. about 310°)	183·8
,,	nitric acid (sp. gr. 1·494, boiled at 165°)	550·
,,	liquid ammonia (sp. gr. 0·978)	865·9
,,	vinegar (sp. gr. 1·007)	905

The following numbers result from the experiments of M. Despretz† :—

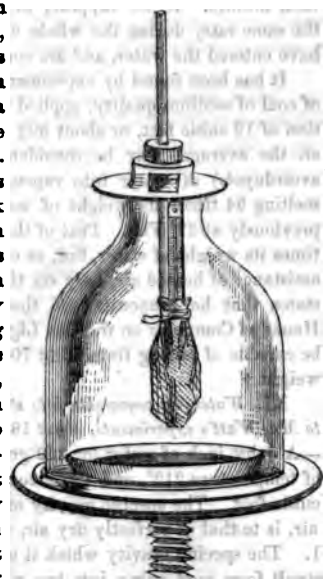
Vapour of water		955°·8
,,	alcohol (sp. gr. ·793)	373°·86
,,	ether (sp. gr. ·715)	163°·44
,,	oil of turp. (sp. gr. ·872)	138°·24

IX. *The absorption of caloric, during evaporation, shown by a very simple experiment.*—Moisten a thermometer with alcohol, or with ether, and expose it to the air, repeating these operations alternately. The mercury of the thermometer will sink at each exposure, because the volatile liquor, during the evaporation, robs it of its heat. In this way (especially with the aid of an apparatus described by Mr. Cavallo in the "Philosophical Transactions," 1781, p. 509) water may be frozen in a thin and small glass ball by means of ether. The same effect may be obtained, also, by immersing a tube, containing water at the bottom, in a glass partly filled with ether, which is to be placed under the receiver of an air-pump; or the ether may be allowed to float on the surface of the water. During the exhaustion of the vessel, the ether will evaporate rapidly; and, robbing the water of heat, will completely freeze it; thus exhibiting the

* "Dict. of Chemistry," page 289. † "Ann. de Chim. et de Phys." xxiv. 329.

singular spectacle of two fluids in contact with each other, one of which is in the act of boiling, and the other of freezing, at the same moment.

By a little modification of the experiment, mercury itself, which requires for congelation a temperature of almost 40° below 0 of Fahrenheit, may be frozen, as was first shown by Dr. Marcet.* A conical receiver, open at the top, is placed on the plate of an air-pump, and a small tube, with a cylindrical bulb at its lower end, containing mercury, is suspended within the receiver, through the aperture, by means of a brass plate, perforated in its centre, and fitting the receiver air-tight, when laid upon its open neck. The tube passes through this plate, to which it is fitted by a leather adjustment, or simply by a cork secured with sealing-wax. The bulb is then wrapped up in a little cotton wool, or, what is better, in a small bag of fine fleecy hosiery, in which a small spirit thermometer, graduated below 40° Fah., may also be included; and, after being dipped into sulphuret of carbon or ether, the apparatus is quickly placed under the receiver, which is exhausted as rapidly as possible.† In two or three minutes the temperature sinks to about 45° below 0, at which moment the quicksilver in the stem suddenly descends with great rapidity. If it be desired to exhibit the mercury in a solid state, common tubes may be used, which have originally been about an inch in diameter, but have been flattened by pressure, when softened by the blow-pipe. The experiment succeeds when the temperature of the room is as high as + 40° Fahrenheit.



X. *The fixation of caloric in water, by its conversion into steam, may be shown by the following experiments:*—1. Let a pound of water at 212°, and eight pounds of iron filings at 300°, be suddenly mixed together. A large quantity of vapour will be instantly generated; and the temperature of the mixture will be only 212°; but that of the vapour produced is also not more than 212°; and the steam must therefore contain, in a latent or combined form, all the caloric which raised the temperature of eight pounds of iron filings from 212° to 300°.

2. When a quantity of water is heated several degrees above the boiling point in a close vessel, and a cock is then suddenly opened, the steam rushes out with prodigious noise and violence, and the heat of the water is reduced in three or four seconds to the boiling temperature. The water, however, constituting the steam which has escaped, amounts to only a very trifling quantity, and yet it has been sufficient to carry off the whole excess of heat from the water in the digester.

3. The quantity of caloric, which becomes latent during the formation of steam, may be approximated, by repeating the following experiment of Dr. Black. He placed

* 34 "Nich. Journ." 119.

† In exhausting a vessel containing either of these fluids, the valves of the air-pump must be metallic.

two cylindrical flat-bottomed vessels of tin, five inches in diameter, and containing a small quantity of water at 50°, on a red-hot iron plate, of the kind used in kitchens. In four minutes the water began to boil, and in twenty minutes the whole was boiled away. In four minutes, therefore, the water received 162° of temperature, or 40½° in each minute. If we suppose, therefore, that the heat continues to enter the water at the same rate, during the whole ebullition, we must conclude that 40½° × 20 = 810° have entered the water, and are contained in the vapour.

It has been found by experiment that 75 pounds of Newcastle coal, or 100 pounds of coal of medium quality, applied in the best manner, are required for the evaporization of 12 cubic feet, or about 89¾ wine gallons of water. In practice, a pound of coal, on the average, may be considered as equivalent to convert a gallon (= 8 pounds avoirdupois) of water into vapour. Wood charcoal, by combustion, is capable of melting 94 times its weight of ice, and of evaporating 13 times its weight of water, previously at 32° Fah. Peat of the best quality, when properly applied, evaporates 10 times its weight of water, but, as commonly used, only 4 or 5 times. Even with the assistance of heated air, only six times its weight can be evaporated, though Curaudau states that he evaporated 25 times its weight.* From evidence given before the House of Commons on the Gas Light Bill, 17¼ pounds of good London coke appear to be capable of raising from 66 to 70 pounds of water into vapour, or about 4 times their weight.†

XI. *Water, by conversion into steam, has its bulk prodigiously enlarged,* viz., *according to Mr. Watt's experiments, about* 1800 *times, or, according to Gay Lussac, only* 1698 *times.* —A cubic inch of water (or 252 grains) occupies, therefore, when converted into steam, of temperature 212°, and force equal to 30 inches of mercury, the space of nearly a cubic foot. The specific gravity of aqueous vapour under the ordinary pressure of the air, is to that of perfectly dry air, taking Gay Lussac's data, as 10 to 16, or 0·62349 to 1. The specific gravity which it ought to have from theory is 0·620, for this should result from condensing, into two volumes, two volumes of hydrogen gas, sp. gr. 0·0688, and one volume of oxygen gas, sp. gr. 1·1025. The experimental result of Gay Lussac was obtained by comparing air and steam at the common temperature of 212° Fah.‡ But as all gases and vapours are expanded or contracted to the same amount by equal variations of temperature, it must be obvious that the same relation will continue between air and aqueous vapour at all other degrees of heat, provided both are subjected to a common temperature and pressure. Steam, therefore, when once formed, derives no greater increase of elastic force, by raising its temperature, than air; and no danger can arise from heating a confined portion of steam, provided the vessel contains no water, from which fresh steam might be generated. In that case, its volume (and if not suffered to expand its elasticity) is increased about one-tenth of the original amount, by every addition of about 50° Fah.

XII. *On the contrary, vapours, during their conversion into a liquid form, evolve, or give out, much caloric.*—The heat given out by the condensation of steam, is rendered apparent by the following experiment:—Mix 100 gallons of water at 50° with 1 gallon of water at 212°; the temperature of the water will be raised about 1¼°. Condense, by a common still-tub, 1 gallon of water, from the state of steam, by 100 gallons of

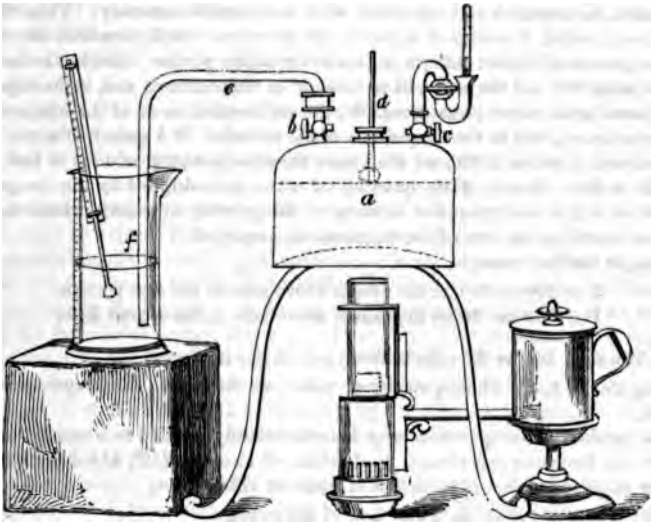
* 79 "Ann. Ch." 86.

† See also Count Rumford's "Researches on the Heat developed in Combustion." Phil. Mag. xli. xlii. and xliii.

‡ "Ann. de Chim. et de Phys.," ii. 135.

water, at the temperature of 50°. The water will be raised 11°. Hence, 1 gallon of water, condensed from steam, raises the temperature of 100 gallons of cold water 9½° more than 1 gallon of boiling water; and, by an easy calculation, it appears that the caloric imparted to 100 gallons of cold water by 8 pounds of steam, if it could be condensed in 1 gallon of water, would raise it to 950°;* and 1 gallon of water converted into steam of ordinary density, contains as much heat as would bring 5½ gallons of ice-cold water to the boiling point. The quantity of ice, which is melted by steam of mean density, is invariably 7½ times the weight of the steam.

For exhibiting the latent heat of steam, by means of a small apparatus, which may be placed on a table, and with the assistance only of a lamp, the boiler represented in the annexed woodcut will be found extremely well adapted. The right angled pipe *e*



must be screwed, however, into its place, and must be made to terminate at the bottom of a jar, containing a known quantity of water of a given temperature. This conducting pipe and the jar should be wrapped round with a few folds of flannel. The apparatus being thus disposed, let the water in the boiler be heated by an Argand's lamp, with double concentric wicks, or any other convenient source of heat, till steam issues in considerable quantity through the cock *c*, which is then to be closed. The steam will now pass through the right angled pipe into the water contained in the jar, which will condense the steam, and will have its temperature very considerably raised. Ascertain the augmentation of temperature and weight; and the result will show how much a given weight of water has had its temperature raised by a certain weight of condensed steam. To another quantity of water, equal in weight and temperature to that contained in the jar at the outset of the experiment, add a quantity of water at 212°, equal in weight to the condensed steam; it will be found, on comparison of the

* "Black's Lectures," i. 169.

two resulting temperatures, that a given weight of steam has produced, by its condensation, a much greater elevation of temperature, than the same quantity of boiling water. This will be better understood by the following example, taken from actual experiment.

Into eight ounces of water, at 50° Fah., contained in the glass jar, *f*, steam was passed from the boiler, till the temperature of the water in the jar rose to 173°. On weighing the water, it was found to have gained 8¼ drachms; that is, precisely 8½ drachms of steam had been condensed, and had imparted its heat to the water. To facilitate the explanation of this experiment, it is necessary to premise the following remarks.

To measure the whole quantities of caloric contained in different bodies, is a problem in chemistry which has not yet been solved. But the quantities of caloric added to, or subtracted from, different bodies (setting out from a given temperature) may, in many cases, be measured and compared with considerable accuracy. Thus if, as has been already stated, 2 pounds of water at 120° be mixed with 2 pounds at 60°, half the excess of caloric in the hot water will pass to the colder portion; that is, the hot water will be cooled 30°, and the cold will receive 30° of temperature; and, if the experiment be conducted with proper precautions, 90°, the arithmetical mean of the temperature of the separate parts, will be the temperature of the mixture. If 3 pounds of water at 100° be mixed with 1 pound at 60°, we shall have the same quantity of heat as before, *viz.*, 4 pounds at 90°. Hence, if the quantity of water be multiplied by the temperature, the product will be a comparative measure of the quantity of caloric which the water contains, exceeding the zero of the thermometer employed.

Thus, in the last example,

$$3 \times 100 = 300 = \text{the caloric above zero in the first portion.}$$
$$1 \times 60 = 60 = \text{the caloric above zero in the second ditto.}$$

The sum, 360 = the caloric above zero in the mixture.

Dividing 360 by 4, the whole quantity of water, we obtain 90°, the temperature of the mixture.

This method of computation may be conveniently applied to a variety of cases. Thus, in the foregoing experiment, 8½ drachms of steam at 212°, added to 64 drachms of water at 50°, produced 72½ drachms of water at 173°. Now,

$$72\tfrac{1}{2} \times 173 = 12542\tfrac{1}{2} = \text{whole heat of the mixture.}$$
$$64 \times 50 = 3200 = \text{heat of 64 drachms, one of the component parts.}$$

$$9342\tfrac{1}{2} = \text{heat of } 8\tfrac{1}{2} \text{ drachms, the other component part.}$$

Therefore 9342½ divided by 8½ = 1099, should have been the temperature of the latter portion (*viz.* 8½ drachms), had none of its heat been latent; and 1099 − 212 = 887 gives the latent heat of the steam. This result does not differ more than might be expected, owing to the unavoidable inaccuracies of the experiment, from Mr. Watt's determination, which states the latent heat of steam, on an average of nine experiments, at 949·9°, say 950°.* Lavoisier, with the aid of the calorimeter, makes it 1000°, or a little more;† Mr. Southern, 945; and Dr. Ure, 967.

XIII. *The same weight of steam contains, whatever may be its density,* (nearly) *the same quantity of caloric; its latent heat being increased,* (nearly) *in proportion as its sensible heat is diminished; and the reverse.*—That portion of the statement which appears in italics, is commonly known as *Watt's law.* Recent investigations have demonstrated that it is

* "Black's Lectures," i., 174, and "Letter to Dr. Brewster," p. 7, n. † Ibid. i. 175.

slightly incorrect, and must now be received, in a philosophical sense, as limited in the text. For all practical purposes, however, the original law of Watt may be considered as unaffected.* This principle, though scarcely admitting of illustration by an easy experiment, is one of considerable importance; and an ignorance of it has been the occasion of many fruitless attempts to improve the economy of fuel in the steam-engine. The fact, so far as respects steam of lower density than that of thirty inches of mercury, was long ago determined experimentally by Mr. Watt.† As the boiling point of liquids is known to be considerably reduced by a diminished pressure, it seemed reasonable to suppose that, under these circumstances, steam might be obtained from them with a less expenditure of fuel. Water, Mr. Watt found, might easily be distilled *in vacuo* when at the temperature of only 70° Fahrenheit. But, by condensing steam formed at this temperature, and observing the quantity of heat which it communicated to a given weight of water, he determined that its latent heat, instead of being only 955°, was between 1200° and 1300°.

The same principle may be explained also by the following illustration, which was suggested by Mr. Ewart. Let us suppose that in a cylinder, furnished with a piston, we have a certain quantity of steam, and that it is suddenly compressed, by a stroke of the piston, into half its bulk. None of the steam will in this case be condensed; but it will acquire double elasticity, and its temperature will be considerably increased. Now, if we either suppose the cylinder incapable of transmitting heat, or take the moment instantly following the compression before any heat has had time to escape, it must be evident that the sensible and latent heat of steam, taken together before compression, are precisely equal to the sensible and latent heat taken together of the denser steam. But in the dense steam the sensible heat is increased, and the latent heat proportionally diminished. Reversing this imaginary experiment, if we suppose only half the cylinder to contain steam at 212°, and the piston to be suddenly raised to the top of the cylinder, the steam will be expanded to twice its volume, its temperature will fall, but its sensible and latent heat taken together will still remain unchanged. The explanation of these facts will be furnished by a principle to be hereafter explained, *viz.*, that the capacities of elastic fluids for caloric are uniformly diminished by increasing their density, and the reverse.

Direct experiments to ascertain the latent heat of steam, formed under higher pressures than that of the atmosphere, have been made by Mr. Southern, of Soho, and by Mr. Sharpe, then of Manchester.‡ Those of the latter were first published, and were to him quite original. They were conceived and executed very ably, but were subsequent, in point of time, to the experiments of Mr. Southern, which, though only lately made public,§ were instituted many years ago. The latter consisted in ascertaining the augmentation of weight and increase of temperature, gained by given quantities of water, from the condensation of known volumes of aqueous vapour of different densities. The results presented differences in the latent heat of steam of different densities, but of so very small an amount as to arise probably from unavoidable sources of error in manipulation. The following table exhibits the principal results obtained by Mr. Southern:—

* See M. Regnault on "Relation des Expériences enterprises pour déterminer les Principales lois et les données Numériques qui entrent dans le Calcul des Machines à Vapeur," Paris, 1847; or a translation of the same in Vol. I. of the Works of the Cavendish Society.

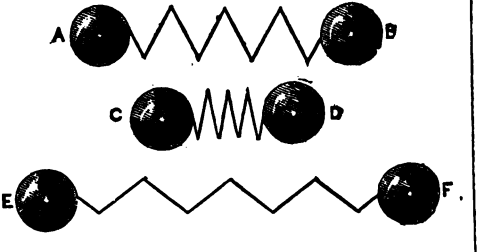
† "Black's Lectures," i. 190. ‡ "Manchester Society's Memoirs," Vol. II., New Series.

§ Brewster's Edition of Prof. Robinson's Works.

Temperature of Steam.	Elasticity of ditto in inches of Mercury.	Latent Heat.
229	40	942°
270	80	942°
295	120	950°

The experiments of Mr. Sharpe, and also a recent series by Clement and Desormes (of which an abstract is given in the Appendix to Thenard's "Traité de Chimie," vol. iv., p. 262, 3me edition), and more recently M. Regnault, establish the same general law, at least within certain limits. This law is of great importance in practice, since it shows that no essential saving of fuel can be reasonably expected from using, as a moving power, steam formed under high pressures: for as a pound of steam, of whatever density, gives out by condensation the same quantity of caloric, it is obvious that, to convert a pound of water into steam, will always require the same quantity of fuel, applied under equal circumstances, whatever may be the density of the steam which is produced. So far, indeed, from tending to economize fuel, it seems probable that the higher the temperature of the water in the boiler, the greater will be the loss of heat by the escape of hot air through the chimney. Nevertheless, there are certain cases in which high-pressure steam may be applied with great advantage to various manufacturing processes, as a means of communicating heat, when the temperature is required to exceed 212° Fah.

A remarkable fact has been observed respecting steam of great elasticity, *viz.*, that when suffered to escape suddenly from a cock or small aperture in the boiler, the hand may be held close to the orifice from which the steam is issuing violently, without being scalded by it, though every one knows that steam of ordinary density scalds severely under the same circumstances. On applying a thermometer to the steam escaping from the boiler, its temperature is found to be considerably reduced: for instance, steam, which, within the boiler, was at 290° Fah., falls suddenly when let out to 160°. That it should fall to 212° would not be surprising, since that is the temperature of steam under the ordinary pressure of the atmosphere; but it is difficult to conceive why it should descend 52° below 212°. Of this fact, Mr. Ewart has given an ingenious, and, it appears to me, a satisfactory explanation, founded on the results of experiments, which he has described in the "Annals of Philosophy" for April 1829. He supposes that the particles of elastic fluids have a tendency, when they are forced near to each other, to fly asunder, not only to their original distance, but beyond it. To illustrate this, let us suppose two equal balls of lead, A B, to be connected by an elastic steel spring, in a perfectly neutral state, so that they have no tendency either to collapse or expand. Compress them nearer to each other, as C and D, and, suddenly setting them at liberty, they will separate, not merely to their original distance, but beyond it, as at E and F. Now, if we suppose A B to represent two atoms of steam, of air, or of any elastic fluid, compressed as C D, and suddenly liberated, they will, by the combined action of their elasticity and momentum, separate to E F, or thereabouts. Thus



high-pressure steam, on suddenly taking off all pressure beyond that of the atmosphere, is converted into low-pressure steam, and its temperature falls, in consequence of the law which connects the rarefaction of elastic fluids with an absorption of caloric. It is quite in accordance with this theory that the more strongly steam is compressed, the more dilated and the colder it is on being suddenly released from pressure.

XIV. *Conversion of Liquids into Vapours under strong Pressure.*—It is well known that by means of a Papin's digester we are enabled to raise the temperature of liquids considerably above the points at which they boil under the mean pressure of the atmosphere; and it seemed probable that the internal pressure, augmenting with the temperature, must effectually prevent the total volatilization of the liquid, especially if the space, left above the liquid, is not of a certain extent. But provided a sufficient space is allowed for the generated vapour, it appeared to M. Cagniard de la Tour, a necessary consequence that there should be a limit beyond which these liquids ought, notwithstanding the pressure, to be completely volatilized; and to verify this opionion he was led to make some interesting experiments.

A strong glass tube, containing about two-fifths its capacity of alcohol, sp. gr. ·837, being carefully heated, the alcohol continued to expand, till, after having attained nearly double its original volume, it was converted into vapour so transparent, that the tube appeared completely empty. Allowing it to cool, the alcohol was again condensed into a liquid. When the proportion of alcohol to the capacity of the tube was increased, the consequence was the bursting of the tube. Similar results were obtained with naphtha and ether, the latter requiring less space than the former for being converted into vapour without breaking the tube; and naphtha less space than alcohol. No difference was occasioned by the presence of atmospheric air in the tubes, or its exclusion from them, except that the ebullition of the liquid was then much more moderate.

The same success did not attend the first attempt to convert water into vapour; for when a tube, about one-third filled with water, was similarly heated, it burst with an explosion. The inner surface of the glass tube appeared also to have been acted upon, its transparency being impaired.

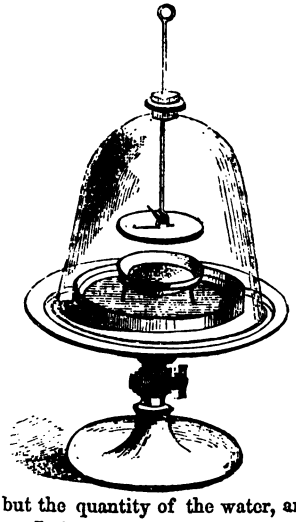
M. de la Tour afterwards determined the densities of these vapours, by means of a gauge which measured the bulk of a confined portion of air, subjected, through the intervention of a column of quicksilver, to the pressure of the generated vapour. Alcohol converted into vapour, and occupying a space a little exceeding three times the volume of the original liquid, he found to exert a pressure = 119 atmospheres, and to require a temperature of 404·6° Fah. Ether, under the same circumstances, required a temperature of 369° Fah., and the force of its vapour was equivalent to 37 or 38 atmospheres; bisulphuret of carbon required 527° Fah., and the pressure of its vapour was equal to 78 atmospheres. Water, to which a minute quantity of carbonate of soda had been added, ceased to act upon glass tubes; and, though several tubes were broken, it was ascertained that water itself may be converted into vapour, provided the vacant space exceed its volume about four times.*

XV. *The evaporation of water is carried on much more rapidly under a diminished pressure, especially if the vapour, which is formed, be condensed as soon as it is produced, so as to maintain the vacuum.*

On this principle depends Mr. Leslie's ingenious mode of freezing water, in an atmosphere of any common temperature, by producing a rapid evaporation from the

* "Ann. de Chim. et de Phys.," xxi. 127, 178; xxii. 410; or "Ann. of Philos.," v. 290.

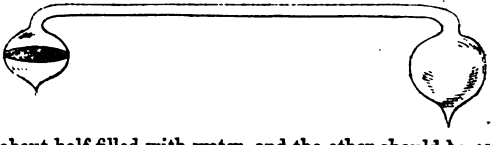
surface of the water itself. The water to be congealed is contained in a shallow vessel, which is supported above another vessel containing strong sulphuric acid, or dry muriate of lime, or even dried garden mould or parched oatmeal. Any substance, indeed, that powerfully attracts moisture may be applied to this purpose. The whole is covered by the receiver of an air-pump, which is rapidly exhausted; and, as soon as this is effected, crystals of ice begin to shoot in the water, and a considerable quantity of air makes its escape, after which the whole of the water becomes solid. The rarefaction required is to about 100 times; but to support congelation, after it has taken place, 20 or even 10 times are sufficient. The sulphuric acid becomes very warm; and it is remarkable, that if the vacuum be kept up, the ice itself evaporates. In five or six days, ice of an inch in thickness will entirely disappear. The acid continues to act till it has absorbed an equal volume of water.



An elegant manner of making the experiment is to cover the vessel of water with a plate of metal or glass, fixed to the end of a sliding wire, which must pass through the neck of the receiver, and be, at the same time, air-tight, and capable of being drawn upwards. (See the annexed figure.) The receiver being exhausted, the water will continue fluid, till the cover is removed, when, in less than five minutes, needle-shaped crystals of ice will shoot through it, and the whole will soon become frozen. If this should not happen, a slight but smart blow, given to the air-pump, will often occasion immediate congelation.

In this interesting process, if it were not for the sulphuric acid, an atmosphere of aqueous vapour would fill the receiver; and this, pressing on the surface of the water, would prevent the further production of vapour. But the steam which rises, being condensed the moment it is formed, the evaporation goes on very rapidly, and has no limits but the quantity of the water, and the diminished concentration of the acid.*

It is on the same principle that the instrument invented by Dr. Wollaston, and termed by him the *Cryophorus*, or *Frost-bearer*, is founded. It may be formed by taking a glass tube, having an internal diameter of about $\frac{1}{4}$th of an inch, the tube being bent to a right angle, at the distance of half an inch from each ball, thus:

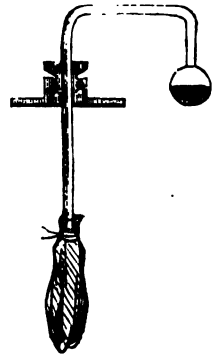


One of these balls should be about half filled with water, and the other should be as perfect a vacuum as can readily be obtained, the mode of effecting which is well known to those accustomed to blow glass. One of the balls is made to terminate in a capillary tube; and when the water in the other ball has been boiled over a lamp a considerable time, till all the air is expelled, the capillary extremity, through which the steam is

* The most complete account of this new mode of freezing is to be found in the Supplement to the "Encycl. Brit.," Art. Cold.

still issuing with violence, is held in the flame of the lamp, till the force of the vapour is so far reduced that the heat of the flame has power to seal it hermetically.

When an instrument of this kind is well prepared, if the empty ball be immersed in a mixture of snow and salt, the water in the other ball, though at the distance of two or three feet, will be frozen solid in the course of a very few minutes. The experiment may be rendered still more striking, if performed according to Dr. Marcet's modification of it: the empty (lower) ball, covered with a little moist flannel, is to be suspended, in the manner shown by the annexed sketch, within a receiver, over a shallow vessel of strong sulphuric acid, and the receiver is then to be exhausted. In both cases, the vapour present in the empty ball is condensed by the operation of cold; and the vacuum, produced by this condensation, gives opportunity for a fresh quantity to arise from the opposite ball, with a proportional reduction of the temperature of its contents.



An ingenious application of the fact that evaporation takes place *in vacuo*, at a lower temperature than under common pressures, was made by the late Mr. Edward Howard, to the concentration of syrup in the process of refining sugar. The syrup, in his method, is inclosed in an air-tight vessel, from which the atmospheric air is extracted mechanically by a pump, and the evaporation, therefore, goes on at a low degree of heat, which secures the syrup from injury.* Mr. J. J. Barry obtains a vacuum in a cheaper and easier manner, by the condensation of steam, applied in a way which would not be understood without a plate, and of which it may be sufficient to say that he can maintain, in the liquid to be evaporated, a steady temperature of from 90° to 100° Fah. Mr. Barry's process is peculiarly adapted to the preparation of medicinal extracts, the active portion of which is liable to be decomposed at a heat considerably below that of boiling water.†

The large quantity of caloric, latent in steam, renders its application extremely useful for practical purposes. Thus, water may be heated, at a considerable distance from the source of heat, by lengthening the conducting pipe *e*. (See page 153.) This furnishes us with a commodious method of warming the water of baths, which, in certain cases of disease, it is of importance to have near the patient's bed-room; for the boiler, in which the water is heated, may thus be placed on the ground-floor, or in the cellar of a house, and the steam conveyed by pipes into an upper apartment. Steam may also be applied to the purpose of heating or evaporating water, by a modification of the apparatus. An apparatus may be made for boiling water by the condensation of steam, without adding to its quantity, a circumstance occasionally of considerable importance. The steam is received between the vessel which contains the water to be heated, and an exterior case; it imparts its caloric to the water through the substance of the vessel; is thus condensed, and returns to the boiler by the perpendicular pipe. An alteration of the form of the vessels adapts it to evaporation. This method of evaporation is admirably suited to the concentration of liquids that are decomposed, or injured, by a higher temperature than that of boiling water, such as

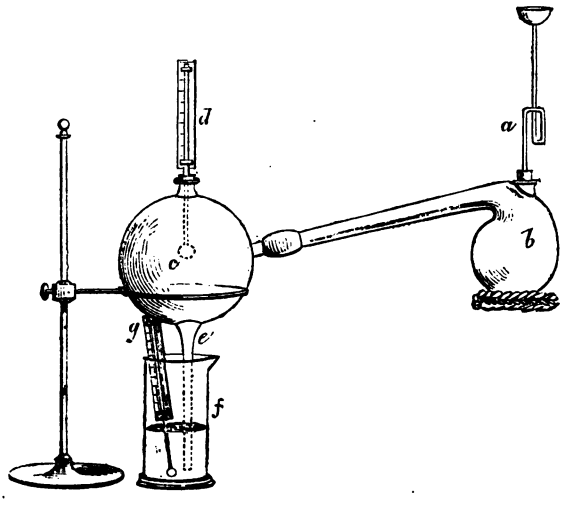
* "Repertory of Arts," Series Two, Vols. XXIII. and XXV.

† See "Transact. of the Medico-Chirurg. Soc. of London," Vol. X.

medicinal extracts; to the drying of precipitates, &c. In the employment of either of these vessels, it is expedient to surround it with some slow conductor of heat. On a small scale, a few folds of woollen cloth are sufficient; and, when the vessel is constructed of a large size for practical use, this purpose is served by the brickwork in which it is placed.

Caloric the Cause of Permanently Elastic Fluidity—General Properties of Gases.—From the facts which have been detailed in the last section, it appears that in vapours, strictly so called, such as the steam of water, caloric is retained with but little force; for it quits the water when the vapour is merely exposed to a lower temperature. But, in permanently elastic fluids, caloric is held very forcibly, and no diminution of temperature that has ever yet been effected can separate it from some of them. Thus the air of our atmosphere, in the most intense artificial or natural cold, still continues in the aëriform state. Hence is derived one character of gases, *viz.*, that they remain aëriform under almost all variations of pressure and temperature, and in this class are also included those aërial bodies which, being immediately condensed by contact with water, require confinement over mercury. The following experiment will show that the caloric contained in gases is chemically combined, or at least that it is inappreciable by the thermometer.

Into a small retort (see annexed cut, *b*) put an ounce or two of well-dried common salt, and about half its weight of sulphuric acid. By this process, a great quantity of gas is produced, which might be received and collected over mercury. But, to serve the purpose of this experiment, let it pass through a glass balloon, *c*, having three openings, into one of which the neck of the retort passes, while from the other a tube, *e*, proceeds, which ends in a vessel of water, *f*, of the temperature of the atmosphere. Before closing the apparatus, let a thermometer, *d*, be included in the balloon, to show the temperature of the gas. It will be found that the mercury, in this thermometer, will rise only a few degrees, whereas the water, in the vessel which receives the bent tube, will soon become almost boiling hot. In this instance caloric flows from the lamp to the muriatic acid, and converts it into gas; but the heat, thus expended, is not indicated by the thermometer. The caloric, however, is again evolved, when the gas is condensed by water. In this experiment we trace caloric into a latent state, and again into the state of free or uncombined caloric.



For demonstrating the influence of variations of atmospheric pressure on the *formation* of gases, better experiments cannot be devised than those of Lavoisier.* But as some students, who have the use of an air-pump, may not possess the apparatus described by Lavoisier (the glass bell and sliding wire), it may be proper to point out an easier mode of showing the same fact. This proof is furnished by the experiment already described, in which sulphuric ether is made to assume alternately an aëriform and liquid state, by removing and restoring the pressure of the atmosphere.

Influence of Atmospheric Pressure.—It was long ago suggested by Mr. Dalton† that all gases are convertible into liquids. "There can scarcely," he observes, "be a doubt entertained respecting the reducibility of all elastic fluids, of whatever kind, into liquids; and we ought not to despair of effecting it in low temperatures, and by strong pressure exerted upon the unmixed gases." It fortunately occurred to Mr. Faraday that the most probable means of exhibiting gases (or rather what, under ordinary circumstances, would be such) in the liquid state, would be to *generate* them under strong pressure; and his experiments have confirmed this sagacious conjecture. When thus produced in strong glass tubes, they continued liquid at low temperatures, while the pressure was kept up, but, on removing the pressure, instantly passed into the gaseous state. Some of them evinced so strong a tendency to become permanently elastic, that the tubes containing them exploded spontaneously, with great violence, by a slight increase of the temperature of the atmosphere. The gases liquefied by Faraday in 1823 were chlorine, euchlorine, sulphureted hydrogen, nitrous oxide, cyanogen, ammonia, and hydrochloric, sulphurous, and carbonic acids. The last-mentioned fluid required for its confinement much stronger tubes than any of the others, and produced the most violent and dangerous explosions.‡

Subsequently to Faraday's experiments, in the year 1823, this philosopher and others have resumed the endeavour to reduce gases to a denser cohesive state, and with the most interesting results. Not only has the number of liquefiable gases been extended to comprehend all except oxygen, hydrogen, nitrogen, nitric oxide, and coal gas, but nine gases have been solidified; they are—

Hydriodic acid.	Oxide of chlorine.
Hydrobromic acid.	Cyanogen.
Sulphurous acid.	Ammonia.
Sulphureted hydrogen.	Nitrous oxide.
Carbonic acid.	

The preceding results warrant the assumption that all gases might be solidified, under a sufficient deprivation of heat; consequently the generalization of a permanently elastic fluid, as applied to a gas, is no longer tenable. It follows, moreover, that, inasmuch as gases evolve latent heat on becoming fluids, and fluids evolve another portion of latent heat on becoming solids, that solidified gases of all substances must absorb the largest amount of heat on assuming their original gaseous state. The first gaseous body ever solidified was carbonic acid. The interesting result was accomplished by M. Thilorier.

In this place I shall confine myself to an indication of the *principles* involved. M. Thilorier accomplished the solidification of liquid carbonic acid by exposing it to the cooling agency of its own evaporation. When produced, the solidified carbonic acid in

* See his "Elements," chap. i. † "Manch. Soc. Mem.," v. 550. ‡ "Phil. Trans.," 1823.

its turn becomes the most powerful agent known to chemists for lowering the temperature of bodies; the method of using it with greatest advantage consisting in mixing it with ether, and forming a bath. It was by the employment of this powerful cooling agent, under the exhausted receiver of an air-pump, and in combination with great pressure, that Faraday, in 1845, made such important additions to the list of gases originally condensed by him in 1823.*

The pressure was effected by means of two force-pumps acting in succession; the first having a piston of an inch in diameter, the second only half an inch. By the first a pressure of about twenty atmospheres was produced; by the second this pressure was increased to more than fifty atmospheres. The tubes used in these experiments were of green bottle-glass, from one-sixth to one-fourth of an inch in external diameter. Three distinct agencies will be recognised as contributing to the general result: (1), the direct cooling agency of the carbonic acid bath; (2), the increased cooling agency of the same under the exhausted receiver; (3), the force of pressure exercised on the gas.

The three tables appended are taken from Gmelin's "Handbuch," and represent the thermometric degree of certain melting and boiling points. It may be well to observe that the melting point of a solid is the freezing or solidifying point of its corresponding liquid. Thus 32° F. is the freezing point of water, as well as the melting point of ice.

In the second table degrees of heat are sometimes represented by the scale of Daniell's and Wedgwood's pyrometer. The latter is a very uncertain instrument, and its manifestations cannot be relied upon. Wedgwood himself estimated the first degree on his instrument as = 598° C., and each degree to 72° C.; Guyton Morveau estimated the first degree at 270° C., and each degree to only 34° C. Connection between the scales of Daniell's pyrometer is effected by graduating the instrument from the fixed point of the boiling of mercury = 662° F. Thus, knowing the amount of linear expansion from any lower degree up to this point, and considering all further expansive increments or decrements as proportional, a scale is formed.

MELTING POINTS.

	Centigrade.	Fahrenheit.
Carbonic acid	— 65°	— 85°
Ether	— 44	— 47·2
Mercury	— 40·5	— 40·9
Oil of vitriol	— 25	— 13
Bromine	— 20	— 4
Hydrocyanic acid	— 15	+ 5
Water	0	+ 32
Phosphorus	+ 45	+ 113
Potassium	+ 58	+ 136·4
Wax	+ 67	+ 152·6
Sodium	+ 90	+ 194
Iodine	+ 107	+ 224·6
Sulphur	+ 109	+ 228·2
Camphor	+ 175	+ 347

* "Phil. Trans." 1845, p. 170; or "Phil. Mag." [illegible]

	Guyton Morveau ("Ann. Chim.," 90, 286).		Wedgwood and Dalton "N. Syst.," 1, 54).		Daniell.		Schwartz.	Rudberg.
	Cent.	Wedgwood.	Cent.	Wedgwood.	Cent.	Daniell.	Cent.	Cent.
Bismuth	·247·	—	247	—	239	66	260	264
Tin	267	—	246	—	227	63	220	228
Lead	312	—	322	—	321	87	340	325
Zinc	374	3	371	—	342	94	500	
Antimony . . .	513	7	432	—			620	
Brass	—	—	—	—	1021	267	Pouillet	Prinsep
Silver	1034	22	—	28	1223	319	1000	990
Copper	1207	27	—	27	1396	364		
Gold	1381	32	—	32	1421	370	1200	
Cobalt	—	—	—	130				
White Cast Iron .	—	—	—	—	—	—	1100	
Gray do. .	4783	130	—	—	1915	497	1210	
Steel	—	—	—	—			1350	
Manganese . . .	5825	160	—	160				
Bar Iron	6346	175					1550	
Nickel Platinum Iridium Rhodium	above	175						
Quartz . . .								

BOILING POINTS.

Sulphurous acid . .	— 10° C.	=	+ 14° Fah.
Hydrochloric ether . .	+ 12	=	+ 53·6
Nitric ether . . .	+ 21	=	+ 69·8
Hydrocyanic acid . .	+ 26·5	=	+ 79·7
Sulphuric ether . .	+ 35·66	=	+ 96·19
Sulphuret of carbon . .	+ 46·6	=	+ 115·82
Bromine . . .	+ 47	=	+ 116·6
Alcohol . . .	+ 78·41	=	+ 173·14
Rock oil . . .	+ 65·5	=	+ 149·9
Water	+ 100	=	+ 212·
Oil of turpentine . .	+ 157	=	+ 314·6
Iodine	+ 180	=	+ 3·56
Camphor . . .	+ 284	=	+ 543·2
Oil of vitriol . . .	+ 288	=	+ 550·4
Phosphorus . . .	+ 250	=	+ 482·
Sulphur . . .	+ 293	=	+ 559·4
Mercury . . .	+ 356	=	+ 672·8
Selenium (nearly) . .	+ 700	=	+1292·

Of Gases under Pressure.—Gases, when once formed, undergo a considerable change of bulk by variations of external pressure. The general law, first, I believe, established on this subject by Mariotte, is, that the *volume of gases is inversely as the compressing force.* If, for example, we have a quantity of gas, occupying, under the common pressure of the atmosphere, 60 cubic inches, it will fill the space of only 30 cubic inches, or one half, under a double pressure; of 20 inches, or one third, under a triple pressure; of 15 inches, or one fourth, under four times the pressure; and so on.

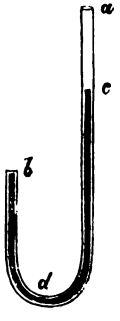
These results, so far as respects the more permanent gases, have been confirmed by Oersted,* who carried the compression of air as far as 110 atmospheres. But with

* "Quarterly Journal," xxii., 193.

respect to some of the more easily liquefiable gases, Despretz has found that they deviate sensibly from Mariotte's law. This is the case with sulphureted hydrogen, sulphurous acid, cyanogen, and ammonia, even when completely deprived of hygrometric moisture.*

The law of the *dilatability of gases by heat* has already been stated to be an enlargement of about $\frac{1}{480}$th part of their bulk for each degree of Fahrenheit's scale, between the freezing and boiling points of water. It is, however, necessary that the gases submitted to experiment should be perfectly deprived of aqueous vapour. These expansions, it has been shown by Sir H. Davy, continue exactly the same in dry, compressed air, at temperatures between 32° and 212°, and also in air confined by columns of quicksilver, whether the air was $\frac{1}{3}$, $\frac{1}{5}$, or $\frac{1}{8}$ of its natural density.†

All gases exhibit a reduction of their temperature by mechanical rarefaction, and an evolution of heat by condensation of their volume. It had long been known that, if a thermometer be inclosed in a receiver, and the air be suddenly condensed, the thermometer rises, and, if the air be rapidly exhausted, it falls; but in each case only a few degrees above or below the temperature of the atmosphere. Mr. Dalton, struck with the *suddenness* of the rise or fall, was the first to suspect that the change of temperature is, in each case, much greater than is indicated by the mercurial thermometer. He contrived, therefore, a very simple and beautiful method of determining the real amount of the change. With this view, he took a large receiver, and inclosed in it a graduated tube, one-fifteenth of an inch diameter, bent siphonwise as in the figure, sealed at the end *b*, and open at the extremity, *a*. Within the tube was a short column of mercury, *c*, the rise or fall of which, by any change of elasticity of the air in the tube, or in the receiver, rendered it a proper *manometer*, or *measurer of rarefaction*. He next doubled the density of the air in the receiver, and of course the mercurial column was forced down till the air in the closed part of the siphon occupied only half its original bulk. Then, suddenly opening the cock attached to the receiver, the mercurial column ran up quickly to its former station. At this moment the cock was suddenly shut, which caused the mercurial column again to fall down gradually for five or ten seconds, to the amount nearly of one-tenth of the column of air included in the manometer, when it became stationary. Once more opening the cock, air rushed out of the receiver, and the mercury regained its position at *c*.



When the experiment was reversed, by exhausting a receiver, under which the same manometer was placed, with the mercurial column stationed at the commencement at *d*, the phenomena took place in a reversed order. At first the mercury rose to *c*; on opening the cock it fell to *d*; on shutting, it retrograded towards *c*; and, on again opening the cock, established itself at *d*.

These facts, which, though observed only with respect to atmospheric air, would, no doubt, take place with some variation in all gases, are explained by Mr. Dalton in the following manner:—

The air in the receiver, and that in the manometer, are subject to a like degree of condensation or rarefaction, or very nearly so. When the equilibrium of heat

* "Ann. de Chim. et de Phys." xxxiv., 335, 443. † "Phil. Trans.," 1823, p. 204.

is disturbed by condensing or expanding the air, it is restored in that within the manometer instantly, by reason of the extensive surface of glass to which that air is exposed. But, in the large receiver, a sensible time, of ten seconds or more, is required to restore the equilibrium through its whole capacity. It is this restoration that increases or diminishes the elasticity of the air in the receiver, and thereby causes the mercurial column to retrograde. Now it is ascertained that, to contract or expand a portion of air by one-tenth of its volume, a change of temperature equal to 50° Fah. is required. It follows, therefore, that in the case of restoring the equilibrium of condensed air, about 50° of cold are produced; and in letting air into an exhausted receiver, 50° of heat are evolved. The phenomena, Mr. Dalton ascertained, are independent of aqueous vapour, and are more remarkable in dry than in humid air. They depend on the diminished capacity of air for heat by condensation, and its increased capacity by rarefaction, and are common to all gases; but, as will appear when we come to speak of the specific heat, vary, as to their extent, in different gases.

When air (and no doubt any other gas) is suddenly and forcibly compressed, in a syringe for instance, the quantity of caloric liberated by the first stroke of the piston is sufficient to set fire to a piece of the tinder called *amadou*. This fact has been applied to the construction of a portable instrument for lighting a candle, consisting of a common syringe, at the bottom of which is a small chamber for containing the tinder. A flash of light is also perceptible in an instrument adapted for showing it by means of a glass bottom, at the moment of condensation.*

All gases, by contact with water, become mingled with aqueous vapour, the proportion of which is regulated by the temperature and pressure to which the gases are subjected; but, those circumstances being equal, *the proportion of aqueous vapour is the same in every gas.* This moisture may be absorbed from gases by substances that strongly attract water, such as quicklime, chloride of calcium which has been recently fused, sulphuric acid, &c.; but to effect this it is necessary that the gas should be confined, and in contact with the absorbent substance, over well-dried mercury.

When a glass vessel, containing any gas not artificially deprived of its moisture, is cooled below the temperature of the atmosphere, moisture is condensed in small drops, or if a freezing mixture be applied, in the form of a thin film of ice, on the inner surface of the vessel. The steam present in gas is also rendered visible by suddenly expanding or suddenly condensing their volume. In the first case, the reduction of temperature which takes place, amounting, as has been shown, to 50° Fah., robs the aqueous vapour of its constituent heat. In the second, the diminution of space, essential to the existence of vapour, causes the precipitation of water, notwithstanding the temperature evolved by condensing the air.

When a body, heated to a certain point, is placed in different gases, under circumstances otherwise similar, it is found to cool with very different velocities; in other words, the *power of elastic fluids to conduct heat differs for different gases.* Dr. Priestley appears to have been quite aware of this; Mr. Dalton has given a series of experiments on this subject; and Sir H. Davy, having raised the same thermometer to the same temperature, 160° Fah., exposed it to equal volumes (21 cubic inches) of the following gases at 52° Fah.

* "Phil. Mag." vols. xiv., xxxi. and xl.

The times for cooling down to 106° were for

	Min.	Sec.		Min.	Sec.
Atmospheric air . .	2	0	Oxygen	1	47
Hydrogen . . .	0	45	Nitrous oxide . . .	2	30
Olefiant gas . . .	1	15	Carbonic acid . . .	2	45
Coal gas . . .	0	55	Chlorine	3	6
Azote	1	30			

It appears from this table that the powers of elastic fluids to abstract or conduct away heat from solid surfaces is in some inverse ratio to their density. The nature of the surface of the hot body, it has been shown by Dulong and Petit, does not affect the conducting power of gaseous bodies; but the state of the gases themselves, as to moisture or dryness, has a considerable influence; for moist gases, as is shown by Count Rumford's experiments, conduct heat much more rapidly than dry ones. Differences, however, in the *specific heats* of gases (if such differences really exist) must render it difficult to determine how much of the effect is owing to that cause, and how much to a real difference of conducting power.

Specific Gravity of the Gases.—Before dismissing the consideration of the gases in general, there are a few properties which it may be proper to notice, with the view of comparing the degree in which they belong to different individuals of the class.

The exact *specific gravity* of the different gases is a most important element in calculating the proportion of the ingredients of compounds into which they enter. Nothing, indeed, can show the importance of this object more strikingly than the fact, that on the precise specific gravities of hydrogen and oxygen gases depend the whole series of numbers which are used to express the weights of the atoms of bodies on the Daltonian theory. The following table exhibits the specific gravities of the most important bodies of this class, on the assumption that 100 cubic inches of atmospheric air weigh 30 grains:—*

TABLE OF THE SPECIFIC GRAVITY OF GASES.

Barometer 30. Thermometer 60°.

Names of Gases.	Specific Gravity.	Weight of 100 cubic inches.	Authorities.
		Grains.	
Atmospheric air	1·0000	30·50	Shuckburgh
Ditto	1·0000	30·199	Brande
Ditto	..	31·	Prout and Dalton
Ditto	..	31·093	Biot and Arago
Ditto	..	31·096	Boussingault and Dumas
SIMPLE GASES AND VAPOURS.			
Oxygen	1·1088	33·82	Allen and Pepys
Ditto	1·1111	33·888	Thomson
Ditto	1·1026	33·626	Berzelius and Dulong

* Gay Lussac's table, which is more copious, but in which the numbers are not reduced to a mean of the barometer and thermometer, is copied into "Thomson's Annals," ix. 16; a table by Professor Wolnecke of Halle is inserted in the "Journal of Science," [illegible]. Dr. Thomson's elaborate paper on this subject is printed in the 18th volume of "Annals of Philosophy;" and Berzelius and Dulong's in the 19th volume of "Annales de Chim. et de Phys." Gmelin's "Handbuch" contains a general tabular exposition of the subject, to which the reader who requires further information is referred. At the present time it is generally admitted that 100 cubic inches of atmospheric air weigh something more than 30 grains; how much more is not yet satisfactorily made out.

Table of Gases continued.

Names of Gases.	Specific gravity.	Weight of 100 cubic inches.	Authorities.
SIMPLE GASES AND VAPOURS.		Grains.	
Chlorine	2·5082	76·500	Davy
Ditto	2·5000	76·250	Thomson
Iodine (vapour)	8·678	244·679	Gay Lussac
Ditto	8·6111	262·6308	Thomson
Hydrogen	0·0694	2·116	Ditto
Ditto	0·0683	2·098	Berzelius and Dulong
Nitrogen	0·9722	29·652	Thomson
Ditto	0·9760	29·768	Berzelius and Dulong
Carbon (vapour)	0·4166	12·6083	Gay Lussac
Sulphur (ditto)	1·1111	33·888	Thomson
Phosphorus (ditto)	0·8333	25·416	Ditto
COMPOUND COMBUSTIBLES.			
Ammonia	0·5960	18·18	Allen and Pepys
Ditto	0·5902	18·003	Thomson
Ditto	0·5912	18·03	Berzelius and Dulong
Carbureted hydrogen	0·5555	16·944	Thomson
Ditto	0·5590	17·049	Berzelius and Dulong
Olefiant gas	0·9722	29·652	Thomson
Ditto	0·9804	29·90	Berzelius and Dulong
Phosphureted hydrogen	0·9027	27·537	Thomson
Bi-hydroguret of phosphorus	0·9722	29·652	Ditto
Sulphureted hydrogen	1·1805	36·007	Ditto
Bi-sulphuret of carbon (vapour)	2·6388	80·486	Ditto
Arsenureted hydrogen	0·5290	16·130	Tromsdorff
Cyanogen	1·8055	55·069	Gay Lussac
Ditto	1·8188	55·473	Berzelius and Dulong
Ether sulphuric (vapour)	2·5808	78·714	Ditto
—— hydrochloric (ditto)	2·2190	67·679	Thomson
—— hydriodic (ditto)	5·4750	166·987	Ditto
—— chloric (ditto)	3·4750	105·257	Ditto
Alcohol (ditto)	1·6004	48·812	Berzelius and Dulong
Turpentine, oil of (ditto)	5·0130	152·896	Gay Lussac
OXIDES.			
Aqueous vapour	0·6250	19·062	Ditto
Nitrous oxide	1·5277	46·597	Thomson
Ditto	1·5273	46·582	Berzelius and Dulong
Nitric acid	1·0416	31·770	Thomson
Carbonic oxide	0·9722	29·652	Ditto
Ditto	0·9727	29·667	Berzelius and Dulong
ACIDS.			
Carbonic	1·5277	46·597	Thomson
Ditto	1·5240	46·481	Berzelius and Dulong
Chlorocarbonic (Phosgene)	3·4722	105·902	Thomson
Chlorocyanic (vapour)	2·1520	65·636	Ditto
Fluoboric	2·3611	72·013	Ditto
Fluo-silicic	3·611	110·138	Ditto
Hydriodic	4·340	132·378	Ditto

Table of Gases continued.

Names of Gases.	Specific gravity.	Weight of 100 cubic inches.	Authorities.
ACIDS.		Grains.	
Hydro-cyanic (vapour)	0·9375	28·572	Thomson
Hyponitrous	2·6382	80·465	Theory
Hydrochloric	1·2847	39·183	Thomson
Nitrous acid	3·1943	97·426	Theory
Nitric	3·75	114·375	Sir H. Davy
Sulphurous	2·2222	67·777	Thomson
Sulphuric (vapour)	2·7777	84·698	Ditto

To the above table I consider it desirable to annex another, deduced by M. Duma from an ingenious and elaborate set of experiments, which form the subject of hi memoir "On some Points of the Atomic Theory," published in the "Ann. de Chim. e de Phys.," xxxiii. 337.

TABLE OF THE DENSITIES (OR SPECIFIC GRAVITIES) OF CERTAIN VAPOURS AND GASES. (AIR = 1.)

Name of Vapour or Gas.	Density by Experiment.	Density by Calculation.
Of Iodine	8·716	8·6118
Mercury	6·976	6·9783
Protochloride of phosphorus	4·875	4·8076
Arsenureted hydrogen	2·695	2·695
Chloride of silicium	5·9390	5·9599
Silici-fluoric acid	3·600	3·5973
Chloride of boron	3·942	4·0793
Fluoboric acid	2·3124	2·3075
Perchloride of tin	9·1997	8·993
——— of titanium	6·836	7·047
Phosphorus	..	2.2052
Arsenic	..	5·1839
Silicium	..	1·0197
Boron	..	0·7487
Tin	..	4·053
Titanium	..	2·107

Since the development of analytical organic chemistry, the problem of determinin the exact weight of 100 cubic inches of atmospheric air, and from it the specific gravit of gases and vapours, has become of increased importance. The problem is not y solved; but we may accept as a fact the statement that 31 grains, or 31·0117, a stated by some authors, Bar. 30", Ther. 60° Fah., is a trifle too low. MM. Biot an Arago, MM. Dumas and Boussingault, are the experimenters on whose deduction relative to this subject chemists of this time place greatest reliance—a reliance whic seems to be warranted not only by the extreme care with which the experiments we conducted, but by the near approximation to coincidence in the result.

According to these philosophers, 1 litre, or 61·02791 cubic inches of air, at 0° Centigrade and 0·76 metres, weigh

	Grammes.	Grains.
Biot and Arago	1·2991	20·063
Dumas and Boussingault	1·2995	20·065

Now, 0·76 metres may be considered equivalent to 30 inches, although more correctly represented by 29·92; and 30 inches is the usual standard of pressure to which, in this country, gases are referred. The zero of Centigrade, however, or the 32nd degree of Fahrenheit, is not our standard to which the temperature of gases is referred, but 60° Fah. Hence, in reducing the previous weights to our standard, it is necessary to make allowance for the increased bulk, or diminished specific gravity, due to the elevation by 28° Fah. Applying, therefore, the rule already stated, namely, that gases expand for every degree of Fahrenheit between 32° and 212° $\frac{1}{480}$th part of their bulk at 32° = (0° C.), or $\frac{11}{30}$ths of every degree of Centigrade between 0° and 100°, we find that at 60° Fah. the one measure (litre) would have expanded to 1·0573 measures, retaining, of course, its original *absolute* weight, but suffering a diminution in specific gravity. Hence, if altered to the conditions of 60° Fah., the weights obtained by MM. Biot and Arago, Dumas and Boussingault, would stand thus:—

At 60° Fah., bar. 30° or (0·76 m.) 1·0573 litres (64·5248 cubic inches) of air weigh—

	Grammes.	Grains.
Biot and Arago	1·2991	20·063
Dumas and Boussingault	1·2995	20·065

Consequently, if 64·5248 cubic inches of air (60° Fah. 30° bar.) weigh 20·063 grains, 100 cubic inches will weigh 31·093 grains, by the proportion

$$64{\cdot}5248 : 20{\cdot}063 :: 100 : \frac{2006{\cdot}3}{64{\cdot}5248} = 31{\cdot}093,$$

which is the weight of 100 cubic inches of air, according to Biot and Arago, at 60° Fah. and 30° bar.; and if 64·5248 cubic inches of air (60° Fah., 30° bar.) weigh 20·065 grains, 100 cubic inches will weigh 31·096 by the proportion

$$64{\cdot}5248 : 20{\cdot}065 :: 100 : \frac{2006{\cdot}5}{64{\cdot}5248} = 31{\cdot}096,$$

which is the weight of 100 cubic inches of air, according to Dumas and Boussingault, at 60° Fah. and 30° bar.

The Specific Gravity of a Gas obtained by Calculation.*—It is usual in a statement of specific gravities, especially of gases and vapours, to mention whether the results are those of direct observation, or whether obtained by calculation. The direct method of taking the specific gravity of a gas has been already detailed (pp. 10, 11).

* The reader will not be unprepared to be informed that in obtaining the specific gravity of a gas by calculation—a process involving, as it does, so many different elements of computation—the results may be slightly different from those deduced from actual experiment. The difference, however, is only, for the most part, in some unimportant decimal place. The theoretical chemist should be informed that the process of actually weighing a gas seldom or never enables the operator to use *with confidence* a smaller weight than the $\frac{1}{100}$th part of a grain. The $\frac{1}{1000}$th may occasionally be employed, when the substance to be weighed is trivial in amount; but this is a condition not usually available in the process of weighing a gas contained, as it must be, in a somewhat heavy flask.

The indirect methods are of various kinds—the two following being the most generally employed, and the most important.

1. Calculated on the data of the specific gravity of hydrogen, the atomic volume of hydrogen and of the gas whose specific gravity is to be determined. This process applies to all gases and vapours, whether simple or compound.

2. Calculated on the data of the specific gravity of components, and the resulting atomic volume of the compound. This process is necessarily restricted to the case of compound gases.

Explanation of Process 1.—It has already been remarked, when discussing the atomic theory and laws of definite combination, that not only do bodies present a mutual relation of combining weights, but of combining volumes also. In gases the truth of the last proposition is directly evident from inspection, and the law is further extended by inferential reasoning. Accepting these data as a starting point, we shall presently see how the specific gravity of a gas may be determined by process No. 1. In the first place, let us assume that all gases possess equal atomic volumes, which is not the case, but the assumption will assist the reasoning process. If this condition be obtained, the atomic or combining volumes of gases might be represented by units of cubic volume, each characterized by a different weight. I have applied the remark to three gases underneath.

Hydrogen	Nitrogen	Chlorine
1	14	35

The weights, it will be observed, are the respective atomic weights of the gases, but they express also the ratio of specific gravity between the same gases; and if hydrogen be taken as the unit of specific gravity for gases instead of atmospheric air, then no further calculation would be required. But if a volume of atmospheric air be taken as the unit of specific gravity for gases, as is usual, then a volume of nitrogen will no longer be fourteen times heavier than unity; a volume of chlorine thirty-six times heavier, &c.; but heavier in the ratio that the second standard of unity (atmospheric air) is heavier than the first (hydrogen). Now the number expressing this ratio is that of the specific gravity of hydrogen referred to atmospheric air as unity. Accepting the specific gravity of hydrogen as 0·0693, which most chemists imagine it to be, this ratio is as follows:—

Representing unity of specific gravity (air) by . . . . S
Specific gravity of hydrogen referred to air by . . . . S'
Atomic weight of gas whose specific gravity is to be determined . w
Undetermined specific gravity of gas by . . . . s

We have

$$S : S' :: w : s = \frac{S'w}{S} = s$$

i.e. the gases of equal atomic volumes, the specific gravity of hydrogen gas multiplied by the atomic weight of the gas whose specific gravity is to be determined, gives its specific gravity.

It so happens that the atomic volumes of hydrogen, nitrogen, and chlorine gases are all equal. Therefore we may now represent the three by cubic figures expressing the

1 : 14 : 35, which other figures are those indicating the respective specific gravi-
as follows:

Hydrogen	Nitrogen	Chlorine
1	14	35
or	or	or
0·0693	·9702	2·425

umbers 0·0693, 0·9702, 2·425, being respectively the products of the atomic weight
e gas to be determined, and the specific gravity of hydrogen.
upposing the gas, whose specific gravity might be desired, possessed only half the
ic volume of hydrogen—as is the case with oxygen—then the ratio would be
sented as follows:—

Hydrogen	Oxygen
1	8 or
or	1·1088
0·0693	

$$\text{Or, } (S : S' :: 2w : x) = \left(\frac{S' \times 2w}{S} = x\right).$$

r, for gases whose atomic volume is half that of hydrogen gas, the specific gravity of gen multiplied by twice the atomic weight of the gas, gives the specific gravity of the

pplying this operation to the present case, we have

$$\frac{0{\cdot}0693 \times (2 \times 8)}{1} = 1{\cdot}1088.$$

gain, supposing the gas, whose specific gravity might be desired, possessed twice omic volume of hydrogen—as is the case with ammonia and many others—then ould have the ratio

Hydrogen	Ammonia
1	15
or	or
0·0693	0·5895

$$\text{Or, } (S : S' :: \frac{w}{2} : x) = \left(\frac{S' \times \frac{w}{2}}{S}\right) = \left(\frac{S' \times w}{2S}\right) = x.$$

r, for gases whose atomic volume is twice that of hydrogen, the specific gravity of gen multiplied by the atomic weight of the gas, divided by two, gives the specific gravity gas.

Applying the operation to the case of ammonia, which is a compound of three atoms of hydrogen and one of nitrogen condensed into two volumes, we have,

	Weight.
Three atoms of hydrogen . .	3
One of nitrogen	14
One atom of ammonia	17

Then, applying the rule, we have $\frac{0{\cdot}0693 \times 17}{2} = 0{\cdot}5895$; hence 0·5895 is the specific gravity of ammonia; air being 1.

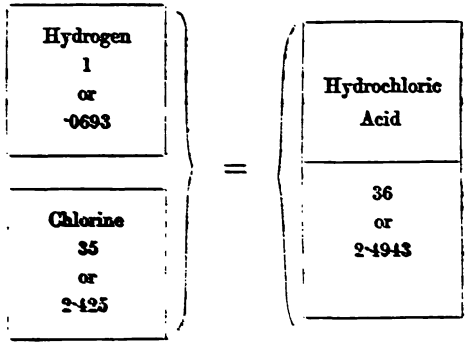
Explanation of Process 2.—The second process of calculating the specific gravity of a gas or vapour, and which applies exclusively to compounds, will readily be understood from the following general description :—If two gases, on combining, experienced no alteration of atomic bulk, then it is evident the mean of the specific gravities of the two components would be the specific gravity of the compound. This is the case when hydrogen unites with chlorine to form hydrochloric acid. Two equal volumes unite without condensation; hence the specific gravity of hydrochloric acid must be the specific gravity of hydrogen, plus the specific gravity of chlorine divided by two, or

Sp. gr. hydrogen	0·0693
Sp. gr. chlorine	2·425
Twice the sp. gr. of hydrochloric acid . .	2·4943

Therefore the sp. gr. of hydrochloric acid is 1·247.

The case may be further illustrated by means of the accompanying diagram—

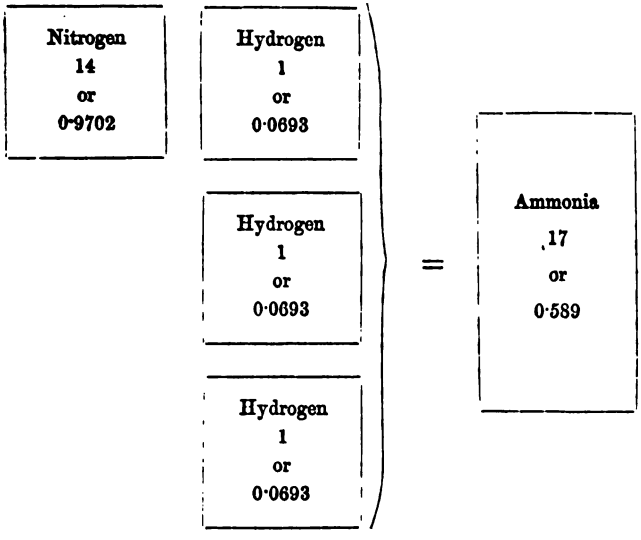
1 vol. of Hydrogen and 1 of Chlorine } unite without condensation and form { 2 vols. of Hydrochloric Acid.



In many instances, however, two gases, when they enter into combination, experience a contraction, differing in ratio for different combinations. Knowing the ratio, and also the specific gravity of the constituents, it is easy to deduce the specific gravity of the resulting compound. For instance—

Three volumes of hydrogen, by uniting with one volume of nitrogen, constitute

ammonia; but the result only occupies two volumes, not four, as represented by the following diagram:—



Hence the specific gravity of ammonia will be the result of the sum of three times the specific gravity of hydrogen and once the specific gravity of nitrogen, divided by two, or

$$\frac{(3 \times \cdot 0693) + 0\cdot 9702}{2} = 0\cdot 589.$$

It is obvious that, as the specific gravity of compound gases may be deduced from a consideration of the specific gravity of their elements and the final volume of combination, so a parallel result may be arrived at by accepting as data the weight of given volumes of component gases and the final volume of the combination. This gives us the weight of a volume of the compound, from which its specific gravity can be deduced. Thus it is evident that, inasmuch as hydrochloric acid is a compound of one volume of chlorine and one volume of hydrogen, without condensation, its specific gravity will be a mean proportional between the sum of the weight of equal volumes of its constituent gases. Now, inasmuch as 100 cubic inches of chlorine weigh 77·33 grains, and 100 cubic inches of hydrogen 0·214 grains, it follows that the weight of 100 cubic inches of hydrochloric acid should be $= \frac{77\cdot 33 + 0\cdot 214}{2} = 38\cdot 55$; whence we deduce its specific gravity by the proportion

$$31 : 38\cdot 55 :: 1 : \frac{38\cdot 55 \times 1}{31} = 1\cdot 24.$$

Properties of Gases.—I. *All solid bodies, that possess a certain degree of porosity, are capable of absorbing gases.*—This was first observed in charcoal, the power of which to condense different gases will be fully described in the section on that substance. It

has been found, also, by Saussure, jun., to belong to a stone called meerschaum, to adhesive slate, asbestos, rock cork, and other minerals; and to raw silk and wool. The following general principles are deducible from the experiments of Saussure.*

1. It is necessary to deprive the solid of the air which it naturally contains. When of a nature not to be injured by heat, this is most effectually done by igniting the solid, and quenching it under mercury, where it is to be kept till admitted to a given volume of the gas to be absorbed. Solids that are decomposable by heat may be deprived, though less effectually, of air, by placing them under a receiver, which must then be exhausted by the air-pump.

2. The same solid absorbs different quantities of different gases. Charcoal, for instance, condenses 90 times its bulk of ammoniacal gas, and not quite twice its bulk of hydrogen.

3. Solids, chemically the same, absorb different quantities of the same gas, according to their state of mechanical aggregation. Thus the dense charcoal of box-wood absorbed 7½ volumes of air; while a light charcoal, prepared from cork, did not absorb a sensible quantity.

4. Different solids absorb different quantities of the same gas; the quantity of carbonic acid absorbed by charcoal being about seven times greater than that absorbed by meerschaum.

5. When the solid exerts no chemical action on the gas, the absorption is terminated in 24 or 36 hours.

6. The effect of moistening the solid is to retard the absorption and to diminish its amount; and when a gas has actually been absorbed it is again driven out unchanged, partly by water of the ordinary temperature, and entirely by exposure to a boiling heat.

7. During the absorption of a gas by a solid the temperature of the latter rises several degrees, and this rise bears a proportion to the absorbability of the gas, and the rapidity with which it is condensed.

8. Solids condense a greater number of volumes of the more absorbable gases under a rare than under a dense atmosphere; but if the absorption be reckoned by weight, it is most considerable under the latter state.

9. When a solid saturated with any one gas is introduced into an atmosphere of any other gas, a portion of the first is expelled, and a part of the second takes its place.

II. *Gases are absorbed by liquids.*—On this subject the following general principles may be laid down:—

1. The same liquid absorbs different quantities of different gases. Thus water takes up its own bulk of carbonic acid, and not one-fiftieth of its bulk of hydrogen gas.

2. Different liquids absorb different quantities of the same gas. Alcohol, for instance, absorbs almost twice as much carbonic acid as is taken up by an equal volume of water.

3. The absorption is promoted by first freeing the liquid from air, either by long continued boiling in a vessel with a narrow neck, or by the air-pump. It requires, also, brisk and long continued agitation, especially with the less absorbable gases.

4. It does not appear that the gases are absorbed by all liquids in the same order. For example, of four gases, naphtha absorbs most olefiant gas; oil of lavender most

* "Annals of Philosophy," vi., 241.

nitrous oxide; olive oil most carbonic acid; and solution of hydrochlorate of potassa most carbonic oxide.

5. The viscidity of liquids, though it does not much influence the amount absorbed, occasions a longer time to be spent in effecting the absorption. On the other hand, the amount of any gas which is absorbed by water, is diminished by first dissolving in the water any saline substance.

6. In general, the lightest liquids possess the greatest power of absorbing gases; whereas, when there is no evident chemical action, the heaviest gases are absorbed most copiously and rapidly by the same liquid.

7. The temperature of a liquid is raised by the absorption of a gas in proportion to the amount and the rapidity of the absorption.

8. In all liquids the quantities of gases absorbed are directly as the pressure. For example, a liquid which absorbs its own bulk of gas under the pressure of the atmosphere, will still absorb its own bulk of the same gas under double, triple, &c. pressure; but its own bulk of gas, twice compressed, is equal to double its bulk of gas ordinarily compressed, and so on. The proofs of this law have been given at length in the "Philosophical Transactions" for 1803, by the late Dr. Henry.

9. When water, or probably any other liquid, is agitated with a limited quantity of any mixture of two gases, it does not absorb one gas to the exclusion of the other, but absorbs a portion of both. In this case, the density of each gas in the water or liquid has a constant relation to that without, *for the same gas.* Thus in carbonic acid gas, the density is the same within and without the water; in olefiant gas and phosphureted hydrogen, the density within is 1-8th of that without; in oxygen and carbureted hydrogen, &c., the density within is 1-27th of that without; in azote and hydrogen, it is about 1-50th, according to Dalton, though he originally stated it to be 1-64th, under the impression that the distances of the particles within were always some multiple of those without. This concise enunciation of the general law, deduced by Mr. Dalton from his experimental inquiries, will be better understood by the illustrations contained in a paper published in the "Annals of Philosophy," vii., 216, where the reader will find a formula for ascertaining the quantities of mixed gases absorbed by water.

The principle on which gases are absorbed and retained by liquids has been a subject of controversy. By Berthollet, Thomson, Saussure, and the generality of chemists, it is ascribed, in all cases, to the exertion of a chemical affinity between the gas and the liquid; but is is contended by Mr. Dalton and myself that the effect in most cases is chiefly, if not wholly, mechanical. The discussion would lead me into details of too great a length; and I refer, therefore, for a full statement of the argument, to two papers which I published in the 8th and 9th volumes of "Nicholson's Journal;" to Mr. Dalton's "New System of Chemical Philosophy;" and to his essay, in the 7th volume of "Dr. Thomson's Annals," which contains a reply to the objections advanced against the mechanical theory by Saussure, in the 6th volume of the same work. This reply seems to have unaccountably escaped the notice of several writers (Berzelius, for instance), who continue to urge the objections of Saussure, after they have been fully and satisfactorily answered by Mr. Dalton. An essay, by Mr. Graham, on the absorption of gases by water, in the 12th volume of "N.S. of Ann. of Phil.," is, however, deserving the reader's attention.

III. *Gases have a mutual tendency to diffusion through each other.*—This operates to such a degree, that, if two different gases are placed in communication, either with

large surfaces, or by a narrow tube connecting two receivers, each containing a different gas, they are found, after a sufficient time, to be intimately mixed. This happens even when the gases have very different specific gravities. In this case the lighter, though placed uppermost at first, gradually descends, and mixes with the heavier, and the reverse. A striking instance of this kind will be given in speaking of hydrogen gas. From the observations of Mr. Faraday, it appears that gases kept over mercury, or in bottles closed by well ground stoppers, gradually exchange places with the external atmosphere, and are not to be relied on for their purity after a long interval of time.*

Döbereiner, Mitchell, and Graham, especially the latter, have also studied the phenomena of mutual gaseous diffusion, which have been referred by Mr. Graham to the agency of one general law, viz. "that the diffusion, or spontaneous intermixture of two gases in contact, is effected by an interchange in position of indefinitely small volumes of the gases, which volumes are not necessarily of equal magnitude, being in the case of each gas inversely proportional to the square root in the density of that gas." Hence the relative diffusiveness of two gases are expressed by the reciprocals of the square roots of their densities. Thus the density of air being 1, its diffusiveness is also 1; the density of hydrogen being 0·0693, its diffusiveness is $\frac{1}{\sqrt{0{\cdot}0693}} = \frac{1}{0{\cdot}2633} = 4{\cdot}56$, the density of ammonia being 0·5898, its diffusiveness is $\frac{1}{\sqrt{0{\cdot}5898}} = \frac{1}{0{\cdot}7681} = 1{\cdot}30$. Hence, if hydrogen and ammonia be placed under circumstances favouring their mutual diffusion, 456 volumes of hydrogen will change place with 1·30 of ammonia; and so on for all other gases.

IV. *Velocity of Gases.*—The velocities with which different gases, when condensed artificially by the same degree of pressure, escape through a capillary tube, has been shown by Mr. Faraday to vary very considerably.† The following table exhibits the comparative times required by some of the gases to escape from a vessel in which they were all equally compressed at the outset, till their density arrived at an atmosphere and a quarter.

Carbonic acid required	156·5 minutes.
Olefiant gas	135·5
Common air	128
Coal gas	100
Hydrogen	57

These differences cease to exist at low pressures; for equal volumes of hydrogen and olefiant gases passed through the same tube, at equal low pressures, in almost the same time. Through small needle holes, hydrogen gas, pressed by a small column of mercury, escaped about three times more quickly than olefiant gas. Increasing the pressure, the same proportions were observed; and also, though not to the same degree, when the gases were expelled through slits cut by a penknife. Both glass and metal tubes produced the effect, and it was heightened as the gas was made to pass more slowly through the tube, and this, whether the increased time was caused by diminished pressure, increased length of tube, or diminished diameter. The specific gravity of the gases seems to have no influence, for carbonic acid, olefiant, and oxygen gases, under the same pressure and other equal circumstances, required respectively 4′ 6″,

* "Quart. Journal," xxii. 358. † "Quart. Journal," iii. 354, vii. 166.

3′ 3″, and 5′ 45″, for the escape of the same quantity of gas; numbers, as will be seen from the foregoing Table of Specific Gravity of Gases, bearing no proportion to their relative weights. What is singular in these results is, that the ratio for the same gas varies with the pressure, and that this variation differs in different gases. Thus the one which passes with the greatest facility at low pressures, passes with the least at high pressures.

This investigation has been pursued and extended by M. Girard.* He was permitted to use, for his experiments, the gasometer and pipes belonging to one of the gas lighting establishments at Paris. The gases operated upon were common air and carbureted hydrogen, which, when allowed to escape at different distances from the gasometer, through equal apertures in a three-inch pipe, and under the same pressure, gave the following results:—

The distances being	1288,	3758,	6228
The quantities of carbureted hydrogen were	1281,	710,	541
Ditto of common air	902,	541,	394

The escape of carbureted hydrogen, therefore, considerably exceeded that of common air, but not in proportion to its inferior specific gravity, which is not much more than half that of the atmosphere, while the excess in the escape of the lighter gas is far from being double that of the heavier. Similar results were obtained when the gases were expelled through tubes of seven lines in diameter, or through an aperture in the side of the gasometer, the lighter gas being discharged in both cases the most abundantly. In the latter case, each gas escaped eleven times faster than when it had to traverse a tube of the same diameter as the hole, and 127 metres in length. In all cases, equal quantities of gas, in any one experiment, escaped in equal times.

These phenomena of the movement of gases through pipes, M. Girard shows, are exactly the same as those of the linear movement of incompressible fluids; and he draws several conclusions, which are important to those practically engaged in operations that require the transmission of gases through long tubes; for which, however, I must refer the reader to the memoir itself.

V. The *colour of the electric spark*, when transmitted through different gases, has been observed by De Grotthus† to be as follows:—

In atmospheric air of double density, the spark was more brilliant, but not coloured.

In hydrogen gas	purple.
— phosphureted hydrogen	red.
— ammonia	red.
— dry carbonic acid gas	violet.
— oxygen gas	violet.
— aqueous vapour	orange.
— vapour of ether } — ditto of alcohol }	celadon green.

The general inference from his experiments is, that the intensity of electric light is always in a direct proportion to the density of the gas, and in the inverse proportion to the conducting power of the gas for electricity.

VI. The *comparative soniferous properties of the gases* have been determined by Messrs. Kerby and Merrick; but, as these belong rather to mechanical than to chemical

* "Ann. de Chim. et de Phys." xvi. 129. † "Ann. de Chim." lxxxii. 34.

science, I shall content myself with referring to the account of them in the twenty-seventh and thirty-third volumes of "Nicholson's Journal," and in the forty-fifth volume of the "Philosophical Magazine;" and to Mr. Leslie's paper on sounds excited in hydrogen gas.*

Of the Apparatus for Experiments on the Gases.—For performing the necessary experiments on gases, many articles of apparatus are essential, that have not hitherto been described. It may assist the student in obtaining the necessary instruments if a few of the most essential be here enumerated. In this place, however, I shall mention such only as are necessary in making a few general experiments on that interesting class of bodies.

The apparatus required for experiments on gases consists partly of vessels fitted for containing the materials that afford them, and partly of vessels adapted for the reception of gases, and for submitting them to experiment.

1. For procuring such gases as are producible without a very strong heat, glass bottles, furnished with ground stoppers and bent tubes, are sufficient. Of these several will be required, of different sizes and shapes, adapted to different purposes. If these cannot be procured, a Florence flask, with a cork perforated by a bent glass tube, or even by a leaden pipe, will serve for obtaining some of the gases.

Those gases that require a red heat for their liberation, may be procured by exposing to that degree of heat the substance capable of affording them, in earthen retorts or tubes; or in a gun barrel, the touch-hole of which has been accurately plugged by an iron pin. To the mouth of the barrel must be affixed a glass tube, bent so as to convey the gases wherever they may be requisite.

A very convenient apparatus, for obtaining such gases as cannot be disengaged without a red heat, consists of a wrought-iron mercury bottle, to which is firmly screwed about two and a half feet of iron gas tube, as represented in the diagram. This iron retort, as it may be called, is particularly useful in the operation of obtaining oxygen by exposing black oxide of manganese to heat.

The extremity (*b*) terminates in a screw, to which a tube of lead or pewter being attached by means of a union fastening, the resulting gas may be conveyed into any convenient receiving vessel.

2. For receiving the gases, glass jars of various sizes, as represented in the diagrams, are required, some of which should be furnished with necks at the top, fitted with ground stoppers (*a*). Others should be provided with brass caps, and screws, [illegible] (*b*). Of these last [illegible] several will be found necessary. [illegible] bladders, or elastic bottles, should be firmly tied, for the

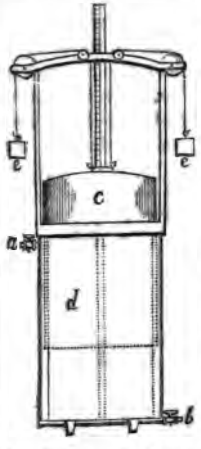
* [illegible]

purpose of transferring gases. These jars will also be found extremely useful in experiments on the properties and effects of the gases. Some of them should be graduated into cubical inches. It is important that jars used for containing gases should be perfectly free from cracks, through which, even when scarcely perceptible, some of the gases, especially hydrogen, have been found by Doebereiner to escape.*

To contain these jars, when in use, a vessel will be necessary, capable of holding a few gallons of water. This may either be of wood, if of considerable size; or, if small, of tin, japanned or painted. Its size may vary with that of the jars employed; and, about two or three inches from the top, it should have a shelf, on which the jars may be placed, when filled with air, without the risk of being overset. In this shelf should be a few small holes, to which inverted funnels may be soldered.

Tubes of various forms and sizes, some of them accurately graduated into hundredths, and others into tenths, of a cubic inch,† are quite essential to those who work much on gaseous substances. Beside these, the experimentalist should be furnished with air-funnels, for transferring gases from wide to narrow vessels.

An apparatus, almost indispensable in experiments on this class of bodies, is a *gasometer*, which enables the chemist to collect and to preserve large quantities of gas, with the aid of only a few pounds of water. In the form of this apparatus there is considerable variety; but, at present, I have no other view than that of explaining its general construction and use. It consists of an outer fixed vessel, *d*, and an inner moveable one, *e*, both of japanned iron. The latter slides easily up and down within the other, and is suspended by cords passing over pulleys, to which are attached the counterpoises, *e e*. To avoid the incumbrance of a great weight of water, the fixed vessel *d* is made double, or is composed of two cylinders, the inner one of which is closed at the top and at the bottom. The space of only about half an inch is left between the two cylinders, as shown by the dotted lines. In this space the hollow vessel *e* may move freely up and down. The interval is filled with water as high as the top of the inner cylinder. The cup, or rim, at the top of the outer vessel, is to prevent the water from overflowing, when the vessel *e* is forcibly pressed down, in which situation it is placed whenever gas is about to be collected. The gas enters from the vessel in which it is produced by the communicating pipe *b*, and passes along the perpendicular pipe marked by dotted lines in the centre, into the cavity of the vessel *c*, which continues rising till it is full, when it is stopped by the cross bar to which the pulleys are attached.

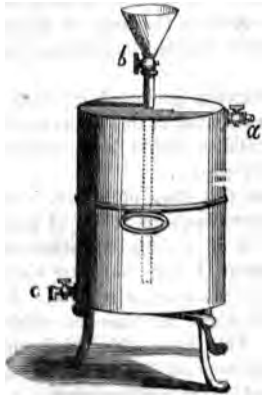


To transfer the gas, or to apply it to any purpose, the cock *b* is to be shut, and an empty bladder, or bottle of elastic gum, furnished with a stop-cock, to be screwed on *a*. When the vessel *e* is pressed down by the hand, the gas passes down the central pipe, which it had before ascended, and its escape at *b* being prevented, it finds its way up a vertical pipe, which is fixed to the outer surface of the vessel, and which is terminated by the cock *a*. By means of an ivory mouth-piece screwed upon this cock, the gas,

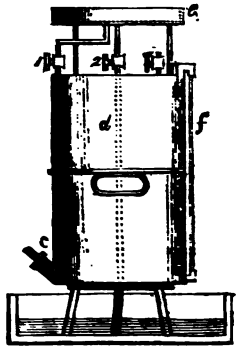
* "Ann. de Chim. et de Phys." xxiv., 332. † See Faraday on Manip. § 112.

included in the instrument, may be respired, the nostrils being closed by the fingers. When it is required to transfer the gas into glass jars standing inverted in water, a crooked tube may be employed, one end of which is screwed upon the cock *b*, while the other aperture is brought under the inverted funnel, fixed into the shelf of the pneumatic trough.

Several alterations have been made in the form of this apparatus, but they are principally such as add merely to its neatness and beauty, and not to its utility; and they render it less easy of explanation. The counterpoises *e e* are now, for example, generally concealed in the framing, and the moveable vessel *c* is frequently made of glass. In some delicate experiments of research, it may be necessary to obtain a current of gas, issuing with a uniform velocity, and under a pressure constantly the same. Such an apparatus was employed by Delaroche and Bérard in their researches into the specific heat of the gases.* Its principle is explained by M. Biot, in his "Traité de Physique," tome i.

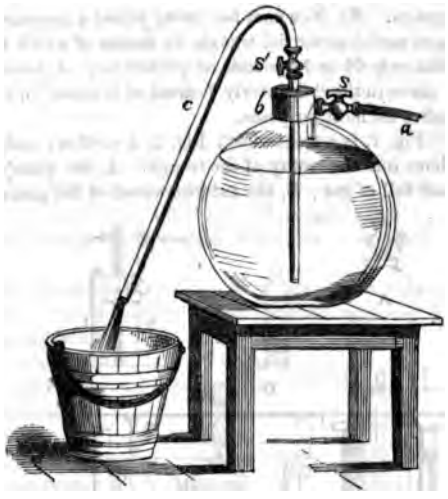


When large quantities of gas are required (as at a public lecture), the gas-holder will be found extremely useful. It is made of tinned iron plate, japanned both within and without. Two short pipes, *a* and *c*, terminated by cocks, proceed from its sides, and another, *b*, passes through the middle of the top or cover, to which it is soldered, and reaches within half an inch of the bottom. It will be found convenient also to have an air cock, with a very wide bore, fixed to the funnel at *b*. When gas is to be transferred into this vessel from the gasometer, the vessel is first completely filled with water through the funnel, the cock *a* being left open and *c* shut. By means of a hroizontal pipe, the aperture *a* is connected with *a* of the gasometer. The cock *b* being shut, *a* and *c* are opened, and the vessel *c* of the gasometer gently pressed downwards with the hand. The gas then descends from the gasometer till the air-holder is full, which may be known by the water ceasing to escape through the cock *c*. All the cocks are then to be shut, and the vessels disunited. To apply this gas to any purpose, an empty bladder may be screwed on *a*, and water being poured through the funnel *b*, a corresponding quantity of gas is forced into the bladder. By lengthening the pipe *b*, the pressure of a column of water may be added; and the gas being forced through *a* with considerable velocity, may be applied to the purpose of a blow-pipe, &c. The apparatus admits of a variety of modifications. The most useful one appears to me to be that contrived by Mr. Pepys, consisting chiefly in the addition of a shallow cistern (*e*, as represented above) to the top of the air-holder, and of a glass register tube, *f*, which shows the height of the water, and consequently the quantity of gas in the vessel.



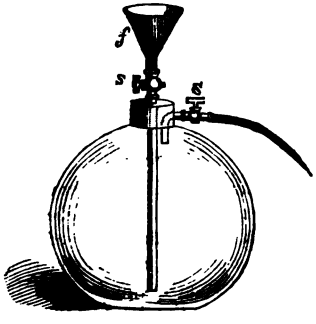
* "Ann. de Chim.," lxxxv. 224.

Perhaps the most convenient vessel for storing oxygen in large quantities, may be formed out of a carboy, as I shall explain.



The carboy itself is furnished with a brass collar *b*, to which are attached two stop-cocks *s* and *s'*. To the stop-cock *s'* is represented in the cut a syphon (*c*) attached. The syphon, however, admits of removal, and is only employed whilst the operation of filling the carboy with gas, *i. e. emptying it of water*, goes on. To the stop-cock *s* is attached a piece of gas-pipe *a*, and this, in its turn, is attached to the wrought-iron bottle, described at page 178.

The arrangement being as described, it is evident that if gas be forced into the carboy through the stop-cock *s*, water will run out through the syphon *c* until the carboy is full of gas.



When filled, the two stop-cocks are turned, the syphon and the tube *a* removed, and a funnel screwed on to *s*, as represented in the annexed cut. The action of the instrument will now be evident at a glance.

If water be poured into the funnel *f*, it follows that gas must emerge through the stop-cock *s*, and thence wherever required. It remains to be stated, that in the diagram the carboy is represented as unprotected. This was done for the sake of securing clearness of illustration; but in practice the carboy is placed on a box in the midst of sawdust, the neck only projecting; the box, moreover, is attached to castors.

The gasometer, already described, is fitted only for the reception of gases that are confinable by water; because quicksilver would act on the tinning and solder of the vessel, and would not only be spoiled itself, but would destroy the apparatus. Yet an instrument of this kind, in which mercury can be employed, is peculiarly desirable, on account of the great weight of that fluid, which makes the employment of large quantities of it both inconvenient and costly; and two varieties of the mercurial gasometer have therefore been invented. The one, of glass, is the contrivance of Mr. Clayfield, and is represented in the plate prefixed to Sir H. Davy's 8vo volume of "Researches," published in 1800. In the other, invented by Mr. Pepys, the cistern for the mercury is of cast-iron. A drawing and description of it may be found in the fifth volume of the "Philosophical Magazine;" but, as neither of these instruments

are essential to the chemical student, and as they are required only in experiments of research, I deem it sufficient to refer to the minute descriptions of their respective inventors. Mr. Newman has lately joined a gasometer of this kind to an improved and most useful mercurial trough, by means of which the advantages of both are obtained with only 60 or 70 pounds of quicksilver. A description and drawing of this apparatus is given in the "Quarterly Journal of Science," i. 186. The following description will suffice for most purposes.

Fig. 1, is a front view; Fig. 2, a section; and Fig. 3, a view looking down from above into the cavity of the trough. A, the glass bell of the gasometer, shown about half full of gas; B, the exterior vessel of the gasometer. In Fig. 1, the central solid

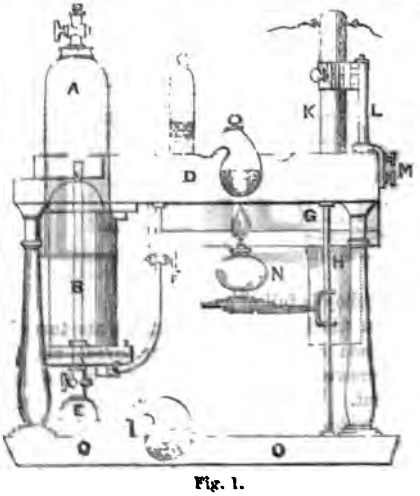


Fig. 1.

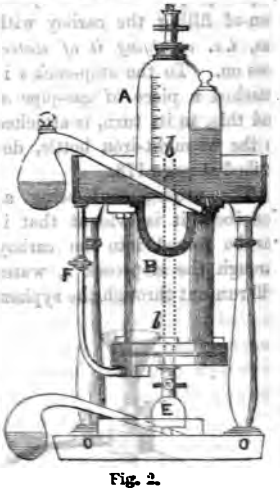


Fig. 2.

part, which fills the cavity of the bell when depressed as far as it will go, is shown by dotted lines, as also is a small iron tube, on which the letter B stands. This tube conveys the gases from the small bell-shaped vessel E, in which they are first received, into the receiver A of the gasometer. In Fig. 2, this tube is marked *b b*, and may be seen rising a little above the mercury, which is thus prevented from falling into it. In Fig. 3, the termination of this pipe is marked by a circle, close to the letter C.

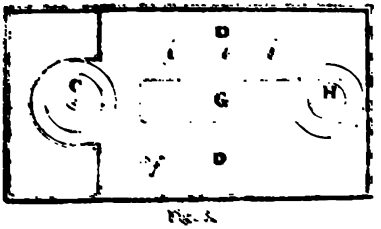


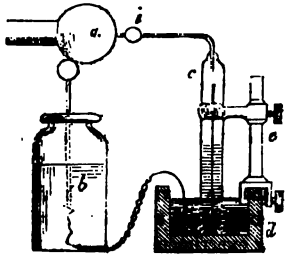
Fig. 3.

D, Fig. 1, one of the sides of the cistern for containing mercury; at G the cistern has a semi-cylindrical cavity seen more distinctly in Fig. 2. F is a small tube opening into the gasometer, and also under one of the small holes *i i*, Fig. 3. By means of this tube, a small portion of gas may, at any time, be transferred from the gasometer into a narrow test tube or other vessel. H is a deep circular cavity, or well, into which a long tube or jar may occasionally be immersed, when it is necessary to have the mercury

at the same level within and without. I, is a receiver into which gas is supposed to be passing from a retort heated by the spirit lamp N. This lamp, by means of a pillar and socket, may be raised or lowered at pleasure, and is secured at any desired height by a spring. K, a Volta's Eudiometer, secured by an upright pillar L, in which is a spring to diminish the recoil on firing any gases. This is moveable, and is fixed when wanted to the side of the trough by the screws M. O O, a sheet iron tray, intended to collect any mercury that may be spilled out of the trough.

For those gases that are absorbed by water, a mercurial trough is necessary. For the mere exhibition of a few experiments on these condensable gases, a small wooden trough, eleven inches long, two wide, and two deep, cut out of a solid block of mahogany, is sufficient; but, for experiments of research, one of cast iron, of considerable size, is required. Very convenient mercurial troughs, on a small scale, are now made of porcelain.

The apparatus required *for submitting gases to the action of electricity*, is shown underneath, where *a* represents the knob of the prime conductor of an electrical machine; *b*, a Leyden jar, the ball of which is in contact with it, as when in the act of charging; and *c* the tube standing inverted in mercury, and partly filled with gas. The mercury is contained in a strong wooden box *d*, to which is screwed the upright iron pillar *e*, with a sliding collar for securing the tube *c* in a perpendicular position. When the jar *b* is charged to a certain intensity, it discharges itself between the knob *a* and the small ball *i*, which, with the wire connected with it, may be occasionally fitted on the top of tube *c*. The strength of the shocks is regulated by the distance between *a* and *i*. By the same apparatus, inflammable mixtures of gases may be exploded by electricity. In this case, however, the jar *b* is unnecessary, a spark received by *i* from *a* being sufficient to kindle the mixture.



The method of *weighing gases* is very simple, and easily practised. For this purpose, however, it is necessary to be provided with a good air-pump, and with a globe or flask *b*, furnished with a brass cap and air-cock. A graduated receiver is also required, to which an air-cock is adapted, as shown underneath.

Supposing a receiver to be filled with any gas, the weight of which is to be ascertained, we screw the cock of the vessel *b* on the transfer plate of an air-pump, and exhaust it as completely as possible. The weight of the exhausted vessel is then very accurately taken, even to a small fraction of a grain, and it is screwed upon the air-cock of the receiver. On opening both cocks, the last of which should be turned very gradually, the gas ascends from the receiving vessel, and the quantity which enters into the flask is known by the graduated scale. On weighing the vessel a second time, we ascertain how many grains have been admitted. If we have operated on common air we shall find its weight to be at the rate of about 31 grains to 100 cubical inches, as already explained. The same quantity of oxygen gas will weigh about 34 grains, and of carbonic acid gas upwards of 47 grains.

In experiments of this kind it is necessary either to operate with the barometer at 30 inches, and the thermometer at 60° Fah., or to reduce the volume of gas employed to that pressure and temperature, by rules which will presently be given. Great care is to be taken, also, not to warm any of the vessels by contact with the hands, from which they should be defended by a glove. On opening the communication between the receiver and the exhausted globe, if any water be lodged in the air-cock attached to the former, it will be forcibly driven into the globe, and the experiment will be frustrated. This may be avoided by using great care in filling the receiver with water before passing into it the gas under examination.

The specific gravity of any gas compared with common air is readily known when we have once determined its absolute weight. Thus, if 100 cubic inches of air weigh 31 grains, omitting fractions, and the same quantity of oxygen gas weighs 34 grains, we say,

31 : 34 :: 1·000 : 1·164.

The specific gravity of oxygen gas will therefore, according to this calculation, be as 1·164 to 1·000. We may determine, also, the specific gravity of gases more simply by weighing the flask, first, when full of common air, and again when exhausted; and afterwards by admitting into it as much of the gas under examination as it will receive; and weighing it a third time. Now, as the loss between the first and second weighing is to the gain of weight on admitting the gas, so is common air to the gas whose specific gravity we are estimating. Supposing, for example, that by exhausting the flask it loses 31 grains, and that by admitting carbonic acid it gains 47; then

31 : 47 :: 1·000 : 1·516.

The specific gravity of carbonic acid is therefore, according to this calculation, 1·516, air being taken at 1·000. And, knowing its specific gravity, we can, without any farther experiment, determine the weight of 100 cubic inches of carbonic acid; for, as the specific gravity of air is to that of carbonic acid, so is 31 (or any other more accurate weight of 100 inches of air) to the number required; or

1·000 : 1·516 :: 31 : 47 nearly.

One hundred inches of carbonic acid, therefore, will weigh about 47 grains.

Practice in Manipulation.—Previously to undertaking experiments on other gases, it may be well for an unpractised experimentalist to acquire manual dexterity by transferring common air from one vessel to others of different sizes, in the following manner:—

1. When a glass jar, closed at one end, is filled with water, and held with its mouth downwards, in however small a quantity of water, the fluid is retained in its place by the pressure of the atmosphere on the surface of the exterior water. Fill in this manner, and invert, on the shelf of the pneumatic trough, one of the jars, which is furnished with a stopper. The water will remain in the jar so long as the stopper is closed; but immediately on removing it, the water will descend to the same level within as without; for it is now pressed equally upwards and downwards by the atmosphere, and falls, therefore, in consequence of its own gravity.

2. Place the jar, filled with water and inverted, over one of the funnels of the shelf of the pneumatic trough. Then take another jar, filled (as it will be of course) with atmospherical air. Place the latter with its mouth on the surface of the water; and, on pressing it in the same position below the surface, the included air will remain in its situation. Bring the mouth of the jar beneath the funnel in the shelf, and incline it

gradually. The air will now rise in bubbles, through the funnel, into the upper jar, and will expel the water from it into the trough.

3. Let one of the jars, provided with a stop-cock at the top, be placed full of air on the shelf of the trough. Screw upon it an empty bladder; open the communication between the jar and the bladder, and press the former into the water. The air will then pass into the bladder till it is filled; and, when the bladder is removed from the jar, and a pipe screwed upon it, the air may be again transferred into a jar inverted in water.

For the purpose of transferring gases from a wide vessel standing over water, into a small tube filled with and inverted over mercury, I have long used the following simple contrivance of Mr. Cavendish. A tube eight or ten inches long, and of very small diameter, is drawn out to a fine bore, and bent at this end, so as to resemble the italic letter *l*. The point is then immersed in quicksilver, which is drawn into the tube till it is filled, by the action of the mouth. Placing the finger over the aperture at the straight end, the tube filled with quicksilver is next conveyed through the water, with the bent end uppermost, into an inverted jar of gas. When the finger is removed, the quicksilver falls from the tube into the trough, or into a cup placed to receive it, and the tube is filled with the gas. The whole of the quicksilver, however, must not be allowed to escape; but a column must be left, a few inches long, and must be kept in its place by the finger. Remove the tube from the water; let an assistant dry it with a towel or with blotting-paper, and introduce the point of the bent end into the aperture of the tube standing over the quicksilver. On withdrawing the finger from that aperture which is now uppermost, the pressure of the column of quicksilver, added to the weight of the atmosphere, will force the gas from the bent tube into the one standing in the mercurial trough.

Rules for Conducting Experiments.—It is necessary to observe the precise quantity of gas at the commencement and close of an experiment, and also that the barometer and thermometer exactly correspond at both periods. An increased temperature, or a fall of the barometer, augments the apparent quantity of gas; and a reduced temperature, or a higher barometer, diminishes its bulk. Another circumstance, an attention to which is indispensable in all accurate experiments, is that the surface of the fluid, by which the gas is confined, should be precisely at the same level within and without the jar. If the fluid be higher within the jar, the contained gas will be under a less pressure than that of the atmosphere, the weight of which is counterpoised by that of the column of fluid within. In mercury, this source of error is of very considerable amount; as any person may be satisfied by raising, above the surface of the quicksilver of a trough, a tube partly filled with that fluid, and partly with air, for the volume of the air will enlarge as the surface of the mercury within the tube is elevated above the outer surface.

In experiments on gases, it is not always possible to begin and conclude an experiment at precisely the same temperature, or with the same height of the barometer; or even to bring the mercury within and without the receiver to the same level. In these cases, therefore, calculation becomes necessary; and, with the view of comparing results more readily and accurately, it is usual to reduce quantities of gas to the bulk they would occupy under a given pressure and at a given temperature. In this country, it is now customary to assume as a standard 30 inches of the barometer, and 60° of Fahrenheit's thermometer, and to bring to these standards observations made under other degrees of atmospheric pressure and temperature. The rules for

these corrections, which are sufficiently simple, have already been given under a different head. A recapitulation of rules, however, will be desirable; they are as follows:—

RULES FOR REDUCING THE VOLUME OF GASES TO A MEAN HEIGHT OF THE BAROMETER, AND MEAN TEMPERATURE.

1. *From the space occupied by any quantity of gas under an observed degree of pressure, to infer what its volume would be under the mean height of the barometer, taking this at 30 inches, as is now most usual.*

This is done by the rule of proportion; for, as the mean height is to the observed height, so is the observed volume to the volume required. For example, if we wish to know what space would be filled, under a pressure of 30 inches of mercury, by a quantity of gas, which fills 100 inches, when the barometer is at 29 inches,

$$30 : 29 :: 100 : 96{\cdot}66.$$

The 100 inches would, therefore, be reduced to 96·66.

2. *To estimate what would be the volume of a portion of gas, if brought to any required temperature.*

If the temperature of the gas is above 32° Fah. multiply its total volume by 490, and divide the product by 490, *plus* the number of degrees that the temperature of the gas exceeds 32° Fah. By this process we obtain the space that the gas would occupy at 32° Fah.

To determine its volume at any other temperature, add $\frac{1}{490}$ of the volume at 32° for each degree that the temperature required exceeds 32° Fah.

Thus, to find what space 100 cubic inches of gas at 50° would occupy if raised to 60,

$$\frac{100 \times 490}{490 + 18} = 96{\cdot}4 = \text{the volume at } 32°.$$

$$\text{And } 96{\cdot}4 + \frac{96{\cdot}4 \times 28}{490} = 101{\cdot}9, \text{ the volume at } 60°.$$

3. In some cases it is necessary to make a double correction, or *to bring the gas to a mean both of the barometer and thermometer.* We must then first correct the temperature, and afterwards the pressure. Thus, to know what space 100 inches of gas at 50° Fahrenheit and 29 inches barometer would fill at 60° Fahrenheit and 30 inches barometer, we first convert the 100 inches, by the second process, to 102. Then, by the first,

$$30 : 29 :: 102 : 98{\cdot}6;$$

or 100 inches, thus corrected, would be only 98·6.

4. *To ascertain what would be the absolute weight of a given volume of gas at a mean temperature, from the known weight of an equal volume at any other temperature.*—First, find by the second process what would be its bulk at a mean temperature; and then say, as the corrected bulk is to the actual weight, so is the observed bulk to the number required. Thus, if we have 100 cubic inches of gas weighing 50 grains at 50° Fahrenheit, if the temperature were raised to 60°, they would expand to 103·6. And

$$103{\cdot}6 : 50 :: 100 : 45{\cdot}4.$$

Therefore 100 inches of the same gas at 60° would weigh 49·02 grains.

5. *To learn the absolute weight of a given volume of gas under a mean pressure, from its known weight under an observed pressure,*—say, as the observed pressure is to the mean pressure, so is the observed weight to the corrected weight. For example,

having 100 inches of gas which weigh 50 grains under a pressure of 29 inches, to know what 100 inches of the same gas would weigh, the barometer being 30 inches,

$$29 : 30 :: 50 : 51{\cdot}72.$$

Then 100 inches of the same gas, under 30 inches pressure, would weigh 51·72 grains.

6. In some cases it is necessary to combine the two last calculations. Thus, if 100 inches of gas at 50° Fahrenheit, and under 29 inches pressure, weigh 50 grains, to find what would be the weight of 100 inches at 60° Fahrenheit, and under 30 inches of the barometer, first correct the temperature, which reduces the weight to 45·4 grains. Then,

$$29 : 30 :: 45{\cdot}4 : 47.$$

One hundred inches, therefore, would weigh 50·71 grains.

Corrections for Moisture in Gases.—Another correction, which it is often necessary to make in taking the weight of gases, is for the quantity of aqueous vapour diffused through them. It is obvious that all gases, which are specifically heavier than aqueous vapour, must have their specific gravity diminished by admixture with steam; and, on the contrary, all gases that are specifically lighter than steam must have their specific gravity increased by that admixture. For the following formulæ we are indebted to Mr. Dalton:—

At ordinary temperatures, the tension or elasticity of aqueous vapour varies from $\frac{1}{100}$ to $\frac{1}{50}$ of the whole atmospheric pressure; in the present case, it is supposed to be a given quantity. The specific gravity of pure steam compared with that of common air, under like circumstances of temperature and pressure, is, according to Gay Lussac, as 0·620 to 1.

Let a = weight of 100 cubic inches of dry common air, at the pressure 30 inches, and temperature 60° Fah.; p = any variable pressure of atmospheric air; and f = pressure or tension of vapour in any moist gas. Then the following formulæ will be found useful in calculating the volumes, weights, and specific gravities of dry and moist gases; putting M for the volume of moist gas; D for that of dry gas; and V for that of vapour—all of the same pressure and temperature.

1. $M = D + V.$ 2. $\frac{p-f}{p} M = D.$

3. $\frac{f}{p} M = V.$ 4. $M = \frac{p D}{p-f} = \frac{p V}{f}.$

If we wish to infer the specific gravity of any dry gas from the observed specific gravity or weight of the same mixed with vapour, it will be convenient to expound p by that particular value which corresponds with a, namely, 30 inches of mercury; and let s = the specific gravity of the dry grass, and w = the observed weight of 100 cubic inches of the moist gas.

Then we shall have the following, *viz.*:

$$5.\quad \frac{30-f}{30} . s\, a + \frac{f}{p} \times {\cdot}620\ a = w.$$

$$6.\quad s = \frac{30}{30-f\,a} \left(w - \frac{f}{p} \times {\cdot}620\ a.\right)$$

EXEMPLIFICATIONS.

1. 98 vol. dry air + 2 vol. vapour = 100 vol. of moist air.

2. Given $p = 30, f = \cdot 5$, and $M = 100$.

$$\text{Then } \frac{p - f}{p} . M = D, \text{ the dry air, } = 98\tfrac{1}{3}.$$

3. And $\frac{f}{p} M = V$, the vapour, $= 1\tfrac{2}{3}$.

4. Given $D = 100, p = 30, f = \cdot 4$.

$$\text{Then } \frac{30 \times 100}{29 \cdot 6} = 101 \cdot 35, \text{ the moist air.}$$

Given $V^* = 2, p = 30, f = \cdot 3$.

$$\text{Then } \frac{30 \times 2}{\cdot 3} = 200, \text{ the moist air.}$$

5. Let $f = \cdot 5, s = 1 \cdot 111, a = 30 \cdot 5, p = 29 \cdot 5$,

$$\text{Then } \frac{30 - \cdot 5}{30} 1 \cdot 111 \times 30 \cdot 5 + \frac{\cdot 5}{29 \cdot 5} \times \cdot 62 \times 30 \cdot 5 = 33 \cdot 64 = w,$$

which gives the specific gravity 1·103.

6. Let f, a, and p, as above, and $w = 2 \cdot 5$, corresponding to sp. gr. 0·8197.

$$\text{Then } s = \frac{30}{29 \cdot 5 \times 30 \cdot 5}\left(2 \cdot 5 - \frac{\cdot 5}{29 \cdot 5} \times \cdot 62 \times 30 \cdot 5\right) = \cdot 07266.$$

The above formulæ apply equally well if V be a permanent gas, or any other vapour beside that of water, the specific gravity of the gas or vapour being substituted instead of ·620, that of steam.

The correction respecting gases, most frequently required in the laboratory, is for moisture; for it is scarcely possible to obtain any gas, artificially deprived of aqueous vapour, in quantity sufficient to be weighed in that state. It is better, therefore, to weigh the gas charged with the full quantity of moisture due to its temperature, which it will soon be if allowed to remain in contact with water; and then to calculate what would be the weight of the same volume entirely free from aqueous vapour. This may be done by the following rule, in exemplifying which 100 cubic inches of moist atmospheric air, at 60° Fah. and 30" bar., are assumed to weigh 31† grains. Find the force of vapour at that temperature by Mr. Dalton's table, which is 0·524.

Then 30 : 0·524 : : 100 : 1·747 = the volume of aqueous vapour in 100 inches of moist air at 60°.

And as 100 cubic inches of aqueous vapour weigh 19 grains, 1·747 cubic inches must weigh 0·3368 grain.

Next, from the weight of 100 cubic inches moist air	31·
Subtract	0·3368
	30·6632

* It is easy to see that V, in this and the other cases, mostly will denote a virtual volume only; or such as would result, if the vapour were condensable like a gas, without being convertible into a liquid.

† In order not to disturb the calculation, this number is allowed to remain; although it is slightly discordant with recent determination of the weight of atmospheric air, which, as we have seen at page 106, is generally admitted to be something more than 31 grains, the point not being as yet made out with more exactness.

We have then the weight of 100 — 1·747 = 98·253 cubic inches dry air, *viz.*, 30·6632 grains.

And 98·253 : 30·6632 : : 100 : 31·214.

The weight, then, of 100 cubic inches dry air, at 30 inches bar. and 60° Fah., is 31·214 grains.

The specific gravity of any other gas compared with common air is then easily determined. For as the weight of 100 cubic inches of dry common air is to the weight of 100 cubic inches of any other dry gas, so is unity to the number required.

Caloric as Occasioning the Spheroidal State of Fluids.—Until the researches of M. Boutigny d'Evreux, philosophers had been accustomed to speak of three conditions of physical state as assumed by bodies in reference to caloric—namely, the conditions of solid, liquid, and vapour, or gas; nevertheless, the phenomenon of *spheroidicity*, or calefaction, as it is sometimes denominated, must have been noticed at periods of very remote antiquity, and, indeed, was probably taken advantage of in the performance of so-called miracles, such as passing the ordeal of fire unscathed, handling molten metals, and other feats of a similar kind. The first person who happened to heat a piece of flint, a morsel of granite, or any metal, and allowed some drops of water to fall upon either of these heated bodies, must have remarked that, under these circumstances, the water would not comport itself as under the more ordinary conditions of applying the source of heat to the solid body having water or other liquid upon its surface from the first. Still, however, the curious phenomena in question do not appear to have been noticed with any view to their generalization until the latter part of the last century, when certain physycists began to analyze the *rationale* of the peculiarity. Amongst the first of these observers was Leidenfrost,* since which time the small number of natural philosophers who have occupied themselves with investigating this phenomenon have scarcely added anything either to the list of experiments bearing upon it or contributed to its theoretic explication. Every person almost has observed, that when some drops of water are allowed to fall upon a capsule made red hot, this water, far from distributing itself over and wetting the metallic surface, assumes the condition of globules, which roll upon the surface without adhering to it. This is the primary fact—this the *point du depart* of M. Boutigny's researches.

In books on physics, writers until lately have contented themselves by saying that water when brought into contact with an incandescent surface, does not adhere to it, but evaporates more slowly than when brought gradually and under ordinary circumstances to the temperature of ebullition; thus leaving the phenomenon itself without any satisfactory explanation.

When a few drops of water are projected upon a slightly concave plate of silver at the ordinary temperature, the liquid moistens the surface of the plate and adheres to every point of contact. If this plate be now heated by means of a spirit lamp or other convenient flame, the water, on being brought to the temperature of 212° Fah., evolves vapour, and, due time being afforded, completely evaporates. But if, before pouring in the water, the capsule be heated considerably above 212°, say to 287 or 288° Fah., then the nature of the resulting phenomenon changes altogether. The water now ceases to adhere to the silver capsule; does not extend over its surface; doubles back on itself, so to speak, and assumes the form of an oblate spheroid. The temperature hitherto fixed at 212° Fah. now suddenly becomes lowered to 212° — x, and remains per-

* De aquæ communis qualitatibus—Duisbourg, 1790.

manently at this degree, notwithstanding the application of any increment of heat. The evaporation, far from being increased by this elevation of temperature, diminishes; water thus circumstanced requiring at least a fifty-fold longer period for the same amount of evaporation than it would if merely subjected to the temperature of ebullition.

Lastly, the oblate spheroid becomes, with peculiar undulatory movements, perfectly visible, and presents the greatest analogy with those produced by sonorous bodies whilst in the act of vibration. The same experiment, repeated with various other liquids, affords, in almost all cases, a similar result, varying only as the normal boiling point varies of the liquid under treatment.

Such are the chief phenomena, such are the new laws which liquids obey, from the period when they cease to be submitted to the ordinary law of equilibrium of temperature,—a law which is only exercised within determinate limits, and a narrow range of conditions.

The following are some experiments by the aid of which the phenomena I have been describing may be rendered sensible. If a portion of some very combustible body be taken—nitrate of ammonia, for example, which inflames at a very low temperature—and if it be projected upon a capsule of platinum, maintained at a red heat, the salt will enter into fusion, will assume the spheroidal condition, will neither burn nor decompose otherwise than very slowly. Remove now the source of heat from the platinum, allow the plate to grow cool to the degree at which the nitrate of ammonia ordinarily inflames, when fusion and combustion will at once take place. This experiment affords a singular example of a very combustible body refusing to burn under circumstances which seem to be most favourable to combustion, and which burns immediately when the excess of heat is removed.

If, instead of nitrate of ammonia, iodine be projected upon the same red-hot plate, the vapours of iodine will be scarcely visible; but if the plate be allowed to cool, the iodine will spread all over its surface, evolving characteristic violet-coloured vapours; and, lastly, if a little distilled water be thrown into a red-hot capsule, the liquid rapidly assumes the spheroidal condition—not adhering to the capsule nor boiling, but evaporating very slowly. If the bulb of a thermometer be plunged into the spheroid, the mercurial column will invariably indicate a lower temperature than that of boiling water; but if the capsule be allowed to cool, the thermometric mercury will at once ascend to 212°, the water will burst into tumultuous ebullition, and will rapidly evaporate in the ordinary manner.

These new and singular facts appear to be in manifest opposition to the known laws of heat; and other experiments, which may be regarded as corollaries of the preceding, may serve to indicate the bearing of these observations.

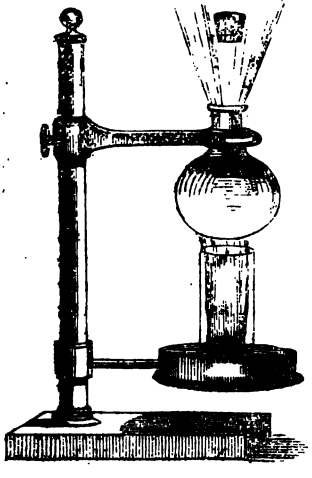
Thus the laws which regulate the demeanour of bodies which have passed into the spheroidal state, may serve to explain certain cases of explosion occurring in steam-boilers. The following experiments will serve to explain the manner in which this accident may occur:—

Take a very thick silver capsule, heat it to whiteness; then seizing it with a pair of tongs, fill it rapidly with water by dipping it into a large vessel containing this liquid; lastly, place the capsule on a support. All the water which it contains is in the spheroidal condition, and, although contained in a vessel heated to whiteness, has only a temperature of 205·3. At length the period arrives when the temperature of the capsule is not sufficient to prolong the spheroidal state, which, passing to the

ordinary condition of liquidity, boils with extreme violence. The apparatus for conducting this experiment is depicted in the subjoined diagram.

The preceding experiment solves, as M. Boutigny justly remarks, a curious problem, which may be thus stated:—*To fill a vessel with water without moistening it, and to boil the water by cooling the vessel.*

The singular phenomena of spheroidicity are not restricted to small masses of liquid, although such have been the subject of my preceding remarks. On the contrary, very large masses of liquid may assume this state, as M. Boutigny has proved. These facts lead to many important practical considerations; pre-eminent amongst which are those having reference to steam-boiler explosions. Anterior to the investigations of M. Boutigny, it was thought that the cause of steam-boiler explosions was the absence of sufficient vent for the overpressure of steam, or the too great increase of fire. M. B—tigny's experiments, however, lead irresistibly to the conclusion that the explosion of a steam-boiler is possible from directly opposite causes—the sudden escape of steam from a boiler by turning a tap; opening a valve or other equivalent means; the sudden removal of fire; by letting in a sudden jet of cold water; or, in short, any act resulting in a lowering of temperature.



The following curious experiment, which admits of ready verification, demonstrates the foundation on which these speculations are based.

A thick silver flask, about the capacity of an oil Florence-flask, being fixed on a very strong iron support, is heated nearly to redness by means of an Argand spirit-lamp. About a fluid drachm of water is now poured in through a tube, and the flask being rapidly and firmly corked, the source of heat is removed. For a short period all remains tranquil. The water introduced having assumed the spheroidal condition evolves but little steam; hence the cork remains tightly fixed. Meantime, the silver vessel gradually cooling assumes a temperature incompatible with the maintenance of aqueous spheroidal fluidity. No sooner has this balance of conditions been attained, than the entire water is at once converted into steam, and the cork is projected with violence. It is easy to trace the connection subsisting between the experiment just described and many conditions to which steam-boilers in action are subjected.

Thus, let it be assumed that a steam-boiler containing its charge of water, and heated in the usual manner, has, for a few instants, all steam egress prevented. In practice such a condition often occurs. Let it now be supposed that a sudden gush of steam takes place, and we shall be in a position to give direct application to the laws of liquid spheroidicity. The first effect of the sudden escape of steam is to cause the charge of water to be projected towards the upper part of the boiler. It falls almost immediately; but, however short the interval between its rising and falling, the boiler itself has been accumulating heat all the while; and this accumulation may be to such an extent that the water on descending no longer comes in contact with the boiler, but assumes the speroidal state. In fact, the boiler and its charge of water are now in almost the identical condition with the silver flask and its charge. The only difference between the two is this:—The silver flask being corked, no issue for the steam existed until the cork was forced out; whereas in the steam-engine boiler, it is assumed that the ordinary working flow of steam takes place. Virtually, however, the steam-engine boiler may be regarded as hermetically closed, as will be demonstrated presently; the area of steam issue being so immeasurably out of proportion to the vast development of steam which ensues when a speroidal mass of water touches the heating surface from which its heat is derived.

Let us now trace out the consequences likely to result. The whole of the water is in the spheroidal state, and an explosion is imminent. Immediate contact between the water and the boiler is cut off—the spheroidal water evaporates with difficulty—the engineer imagines this paucity of steam depends on too little fire—more fuel is, consequently, thrown into the furnace, and the boiler continues to acquire more heat. Under these conditions, an explosion will almost infallibly be determined by one of two circumstances—namely, the sudden withdrawal of fuel, or the sudden addition of a jet of cold water to the boiler charge, either of which is attended with a diminution of temperature, the result of which has already been indicated. It was remarked, that virtually no difference of conditions existed between the steam-engine boiler, as I have assumed it, and the silver flask experiment just described. The justice of this statement will be at once seen from the following calculation:—

Suppose, for the sake of example, the capacity of a steam boiler to be 100 quarts, gallons, or any other assumable quantity. Suppose it only contains ten parts of water, which water exists in the spheroidal state. Suppose the temperature of the boiler to have risen to 1112° Fah., or 1260° Fah., as it might under the conditions assumed, the temperature of the spheroidal water being only 205·6° Fah. Suppose now a mass of cold water be suddenly turned into the boiler, and sufficient in amount to destroy the spheroidal state of the water previously existing there. At that moment there will be formed no less than *seventeen thousand measures* of vapour, which, undergoing still further expansion by contact with the sides of the boiler, will develop all but irresistible force. The explosion here assumed to take place may also be occasioned by sudden removal of the fire, or, as was the case in the silver flask experiment, by the gradual cooling of the boiler, although, in practice, various circumstances contribute to diminish the probabilities of accident from the latter cause. Not only, as M. Boutigny justly remarks, is there danger from the pressure of steam in these cases, but also from the decomposition of a portion of water, oxygen uniting with the iron of the boiler, and hydrogen being liberated. This result always ensues when water assumes the spheroidal condition in an iron vessel heated to incipient redness, or even a still lower temperature.

Supposing the boiler to belong to a marine engine which cannot be stopped, the precautionary means would consist in maintaining a powerful fire, and introducing to the boiler small charges of water at a time. If the phenomenon manifests itself on land, then the engine should be at once stopped, a good fire being kept up, and the boiler emptied of its water with all possible dispatch; finally, a current of air should be driven through the boiler, for the purpose of removing a certain amount of hydrogen gas which will always be found there under the circumstances.

Prevention of steam-boiler explosions from this cause.—It will have been gathered, from the consideration of previous remarks, that inequality of stoking, and inequality of water-supply are amongst the causes determining the spheroidicity of water in steam-engine boilers; from which will be seen the importance of obviating these sources of danger, should they exist. Other means of safety may be deduced from a consideration of the following circumstances.

1. *Ceteris paribus*, the facility with which liquid spheroidicity is assumed, is proportionate with the smoothness of surface of polish of the heating solid. It is fortunate, then, that in the ordinary result of manufacture, steam-engine boiler plates are never polished; were they so, doubtless their explosion would be a much more frequent occurrence than at present. Following out the idea of roughness, M. Boutigny refers the effect to the existence of increased surface. He first thought of bristling the interior of steam boilers with points, but gave up the idea on account of many insuperable objections: not to its theory, which is correct, but to its practice. Ultimately he was led to adopt a boiler divided into many compartments by metallic diaphragms. This kind of boiler has already been applied in practice; it cannot be exploded by causes dependent on fluid spheroidicity, and seems, in other respects, to present many advantages.

2. *Ceteris paribus*, the presence of soluble saline bodies diminishes the tendency to spheroidicity; or, perhaps, it may be more correct to say that the temperature at which spheroidicity ensues must be greater. Hence, *ceteris paribus*, marine engines are not so liable to suffer from this cause as land engines.

Relation of Caloric to the Spheroidal State.—This part of the subject resolves itself into an investigation of the following points:—

1. The lowest degree of temperature at which the phenomenon can occur.
2. The law of evaporation in the spheroidal state.
3. The temperature of bodies in the spheroidal condition, and the temperature of their vapour.
4. Whether radiant caloric traverses the spheroids or is radiated from them.
5. Whether all bodies are susceptible of passing into the spheroidal state.
6. Whether there be contact between liquids in the spheroidal state and the surfaces which gave rise to them.

As regards the first point,—the lowest degree of temperature at which the spheroidal condition can be assumed by water,—M. Boutigny has proved, contrary to the expressed opinions of many physycists, that luminous heat is unnecessary. He has proved that as regards water on platinum, the phenomenon can manifest itself even at so low a degree as 171° Cent. = 339·8° Fah., although at this temperature the demonstration is attended with difficulties. For other substances the temperature varies, always being above their respective boiling points; but according to no ratio yet discovered.

The law of evaporation of water and other liquids in the spheroidal condition is this:—whatever the ordinary boiling point of a liquid may be, its spheroidal evaporation point is something less; but the ratio of diminution has not yet been discovered. M. Boutigny has determined the evaporating point of water in the spheroidal state to be 96·5° C. = 205·7° Fah.; and the evaporating point under similar conditions of four other fluids as follows:—

	C.		F.
Absolute alcohol . . .	+ 75·5°	=	+ 167·9°
Oxide of ethyle . . .	+ 34·25°	=	+ 93·65°
Chloride of ethyle . . .	+ 10·5°	=	+ 14·9°
Sulphurous acid . . .	− 10·5°	=	+ 50·9°

Those respective temperatures at which spheroidal evaporation of each liquid ensues are, *ceteris paribus*, invariable, notwithstanding any excess of temperature which may be imparted to the heating surface.

Does radiant heat traverse the spheroids, or is the heat reflected from them? In opposition to the opinions of philosophers who preceded him, M. Boutigny adopts the second hypothesis. His views are supported by the following experiments, and others of similar bearing:—

If a capsule of platinum be heated to redness and a little water be dropped in, the water immediately assumes the spheroidal state. If now a small glass bulb containing a little water be immersed into the spheroid, the water will not boil, which it should have done, had the radiant heat darted off from the red-hot platinum crucible permeated the aqueous spheroid. The period of contact between the experimental bulb and the spheroidal fluid may be longer delayed, and, consequently, the result more conveniently observed by using, instead of simple water, as the fluid to assume spheroidicity, a mixture of water and lamp-black, well incorporated.

Perhaps, however, the most remarkable experiment in support of the hypothesis is this:—On heating a silver capsule, as already described, and dropping in a little nitric acid; the latter immediately assumes the spheroidal state, in which condition—as will be hereafter shown—there is no contact between the two, and hence no action. If now the spheroid of nitric acid be caused to roll about over the surface of the capsule, the observer will notice that every part of silver, corresponding to its path, will glow more than the other parts; a result which seems to prove that heat is reflected from the under surface of the spheroid back again.

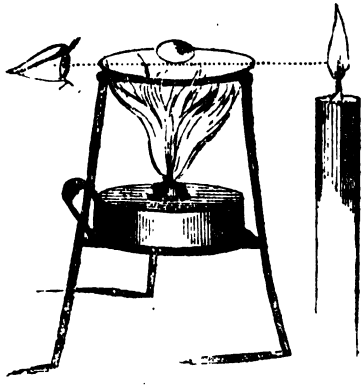
It is a remarkable fact in connexion with these experiments, that particles of sand, filings of metal, and other heavy substances, when thrown upon a spheroidal mass of liquid, do not sink through it, as would seem accordant with the laws of gravitation, but envelop it.

Are all bodies susceptible of passing into the spheroidal state? Experiments seem to answer this question in the affirmative, although the facility of assuming this state for various bodies varies between wide limits.

Does contact ensue between bodies in the spheroidal state, and surfaces which generated this condition? This question may be resolved in the negative, by a readily performed experiment, which, however, must take place in a darkened room:—

A lamina of polished silver, made convex in the slightest degree, only sufficient to prevent any liquid running off after being placed upon it, is heated to incipient redness

ans of an eolipile, or spirit blow-pipe, with vertical jet. A few drops of water w poured upon the heated plate. The water immediately assumes the spheroidal ion, and can be proved to be absolutely separated from the heated silver, by g a candle-flame on the level of the surface, as represented by the dia- The candle-flame will be perfectly t. The separation of the spheroidal from its generating surface being rendered evident, the cause of its tion remains to be determined. M. at advances the opinion that the sepa- is attributable to interposition of r. M. Person agrees in this opi- but M. Boutigny advances one of n, which is supported by evidence so ful, that it is to me convincing. This pher attributes the separation to the ve agency of heat; and he cites the ing experiment as negativing the ition that the spheroid is supported



interposition of vapour. Instead of a platinum capsule, take a flat helix of platinum wire, and press it into the capsular form. Heat the helix by a spirit-lamp, and drop upon it a little alcohol. The liquid immediately assumes the condition of spheroidicity, and remains detached from the wires, as it would have done from a solid capsule. Evidently no upward pressure of vapour—M. Boutigny argues—can exist under the conditions specified, such vapour having free egress through the spaces between each coil of the wire. That it escape can be demonstrated by setting fire to it underneath.

still more remarkable demonstration of the separation of bodies in the spheroidal from the generating surface, is afforded by the celebrated experiment of freezing in a red-hot platinum crucible, the discovery of which remarkable effect was as s:—

quid anhydrous sulphurous acid boils under ordinary circumstances at about h. M. Boutigny was desirous of studying this material under the condition of idicity; and, having poured a little into a red-hot platinum crucible, he was sur- to find that occasionally the acid became opalescent. Eventually he discovered arise from moisture existing in the surrounding atmosphere. He found the cent material to be ice; and, by slightly altering the experiment, he pro- ice in solid cakes. Instead of relying upon atmospheric moisture, he poured drops of water upon the spheroidal sulphurous acid. The water immediately

a slightly-moistened hand be plunged into molten iron, lead, or other metal, rithdrawn with moderate rapidity, not the slightest injury will be expe- d. Usually the natural moisture of the skin is sufficient; but, to ensure safety, nd, previous to immersion, should be rubbed with a moist cloth. The only points ttended to in performing these experiments are to avoid dashing the hand into olten mass, to be sure the latter be at a temperature greatly above its consolidating

point, and to operate with short nails. The experiment, though perfectly harmless, appears so frightful, that it is some little time before even a philosopher can be induced to perform it. Nevertheless, there is reason to believe that feats of a similar kind have been performed at periods of very high antiquity. The impunity with which the act is performed follows as the inevitable result of that law of spheroidal fluidity which determines an absolute separation between a body sufficiently heated, and moisture in its vicinity. The hand becomes invested with a layer of spheroidal fluid, through which the heat cannot penetrate.

Researches relative to the spheroidal state may lead, as M. Boutigny remarks, to the explanation of many recorded miracles of the ancient and middle ages. Thus, in the year 241, Sapor, or Chapour, ordered the Magi to do all in their power to bring back to the religion of their fathers certain seceders. One of the High Priests of the dominant religious order proposed that the truth or falsehood of the religious schism should be determined according to the result of a fiery ordeal on his own person. He proposed that eighteen pounds of molten copper should be poured upon his naked body; and that if he came forth unscathed, the seceders should accept the miracle as a proof that their dogmas were false. The priest, we are informed, submitted to the ordeal; and not being in any degree injured, the seceders were all converted.

The marvellous tales of ordeals by fire during the middle ages—of incombustible men, who could run, unharmed, barefooted over glowing iron—who could plunge their hands with impunity into molten iron or lead, and apply glowing iron to their tongues—are probably true. The feats seem miraculous; yet the real miracle would be a contrary result.

Specific Caloric.—Equal weights of the *same* body, at the same temperature, contain the same quantities of caloric. But equal weights of *different* bodies, at the same temperature, contain unequal quantities of caloric. The quantity of caloric which one body contains, compared with that contained in another, has been considered by Dr. Irvine and others to be proportional to their *specific heats*, a term employed, by him and by others, to denote the quantity of caloric which a body requires, in order to be heated a single degree, or through a certain number of degrees, relatively to that required by any other body to produce the same change. The method of determining the *specific heat or specific caloric* of different bodies is as follows:—

It has already been observed, that equal weights of the *same* body, at different temperatures, give, on admixture, the arithmetical mean. Thus, the temperature of a pint of hot water and a pint of cold, is, after mixture, very nearly half way between that of the two extremes. But this is not the case when equal quantities of *different* bodies, at different temperatures, are employed.

(*a*). If a pint of quicksilver, at 100° Fah., be mixed with a pint of water at 40°, the resulting temperature will not be 70° (the arithmetical mean), but only 60°. Here the quicksilver loses 40° of heat, which nevertheless raise the temperature of the water only 20°: in other words, a larger quantity of caloric is required to raise the temperature of a pint of water than that of a pint of mercury, through the same number of degrees. Hence it is inferred, that water has a greater capacity for caloric than is inherent in quicksilver.

(*b*). The experiment may be reversed by heating the water to a greater degree than the quicksilver. If the water be at 100°, and the mercury at 40°, the resulting temperature will be nearly 80°; because the pint of hot water contains more caloric than is necessary to raise the quicksilver to the arithmetical mean.

(*c*). Lastly, if we take two measures of quicksilver to one of water, it is of no consequence which is the hotter; for the resulting temperature is always the mean between the two extremes; for example, 70°, if the extremes be 100° and 40°. Here, it is manifest, that the same quantity of caloric, which makes one measure of water warmer by 30°, is sufficient for making two measures of quicksilver warmer by the same number. Quicksilver has, therefore, a less capacity than water for caloric, in the proportion, when equal measures are taken, of one to two.

If, instead of equal *bulks* of quicksilver and water, we had taken equal *weights*, the disparity between the specific caloric of the mercury and water would have been still greater. Thus, a pound of water at 100°, mixed with a pound of mercury at 40°, gives a temperature of $97\frac{1}{4}$°, or $27\frac{1}{2}$° above the arithmetical mean. In this experiment, the water, being cooled from 100° to $97\frac{1}{4}$°, has lost a quantity of caloric reducing its temperature only $2\frac{1}{4}$°; but this caloric, communicated to the pound of mercury, has occasioned, in its temperature, a rise of no less than $57\frac{1}{2}$°. Therefore, a quantity of caloric, necessary to raise the temperature of a pound of water $2\frac{1}{4}$°, is sufficient to raise that of a pound of mercury $57\frac{1}{2}$°; or, by the rule of proportion, the caloric which raises the temperature of a pound of water 1°, will raise that of a pound of quicksilver about 23°. Hence it is inferred, that the quantity of caloric contained in water is to that contained in the same *weight* of quicksilver as 23° to 1°. Or, stating the caloric of water at 1°, that of quicksilver will be $\frac{1}{23}$ part of 1°, or 0·0435.*

In a similar manner may the specific heats of other bodies be ascertained. If a pound of water at 100°, and the same weight of oil at 50°, be mixed, the resulting temperature is not 75° (the mean), but $83\frac{1}{3}$°; the water, therefore, has lost only $16\frac{2}{3}$°, while the oil has gained $33\frac{1}{3}$°. Or, if equal weights of water at 50°, and oil at 100°, be mixed, the resulting temperature is $66\frac{2}{3}$°, so that the oil has given out $33\frac{1}{3}$°, and the water has increased only $16\frac{2}{3}$°.† Hence the heat which raises a given weight of water 1°, will raise the same weight of oil 2°; and, as the specific heats are inversely as the changes of temperature, the specific heat of water may be called 1, and that of oil 0·5.

In some instances, it is not possible intimately to mix together the bodies under examination. When the specific heat of a solid mass of metal is to be ascertained, it may be heated throughout to a certain degree, and then surrounded by water of 32°, observing the increase of temperature which is gained by the water, and calculating the specific heat in the same manner as before. This was the method of Wilcke; but Lavoisier and Laplace substituted ice for water, placing, by means of an apparatus called the *Calorimeter*, the heated body in the centre of a quantity of ice, and determining the caloric evolved by the quantity of ice melted in each instance.

When this comparison is extended to a great variety of bodies, they will be found to differ very considerably in their capacities for caloric. The results of numerous experiments of this kind are comprised in a table of specific caloric.

The capacities of bodies for caloric influence considerably the rate at which they are heated and cooled. In general, those bodies are most slowly heated, and cool most slowly, which have the greatest capacities for heat.‡ Thus, if water and quicksilver be set in similar quantities, and at equal distances, before the fire, the quicksilver

* The above numbers, which differ from those commonly stated, are given on the authority of Dr. Dalton.

† Dr. Thomson's "Chemistry," vol. i.

‡ See Martine on "Heat," p. 74.

will be much more rapidly heated than the water; and, on removal from the fire, it will cool with proportionally greater quickness than the water. By ascertaining, then, the comparative rates of cooling, we may determine, with tolerable exactness, the specific caloric of bodies.

It has been doubted whether the specific heats of bodies are permanent so long as they retain their form; in other words, whether a quantity of heat, which raises a body through a certain number of degrees at any one temperature, will raise it through an equal number of degrees at other temperatures. This subject, to which Mr. Dalton had formerly turned his attention,* has been lately investigated more completely by Petit and Dulong.† They heated the body to be tried to the required temperatures, and ascertained what number of degrees of heat it communicated to a certain quantity of water. Repeating these trials at various points of the thermometric scale, they found that the specific heats of bodies are greater at high than at low temperatures. Thus the specific heat of iron was found to be as follows:—

Centigrade.	Specific heat.
From 0 to 100°	0·1098
„ 0 to 200°	0·1150
„ 0 to 300°	0·1218
„ 0 to 350°	0·1255

The same law was found to extend to various other bodies, as is shown by the following table:—

	Specific heats between 0° and 100° Cent.	Specific heats between 0° and 300° Cent.
Mercury	0·0330	0.0350
Zinc	0·0927	0·1015
Antimony	0·0507	0·0549
Silver	0·0557	0·0611
Copper	0·0949	0·1013
Platinum	0·0355	0·0355
Glass	0·1770	0·1900

Another law, deduced by Petit and Dulong, from their researches on heat, is, that *the atoms of all simple bodies have precisely the same specific heat.* This, however, is to be considered, at present, merely in the light of an ingenious speculation, derived from a train of reasoning, a defect in any part of which must be fatal to the conclusions.‡ In the following table, the specific heats of certain bodies, found by the method of Delaroche and Bérard, Regnault, Naumann, Delarive, and Marcet, is given, together with the weights of the atoms of those metals, and the products of the specific heats and weights of atoms.

If the preceding induction should prove to be correct, the chemist will be furnished with another means of testing the accuracy of atomic weight for any given body. Indeed, this sort of calculation has already been followed; but much yet remains to be proved as regards the original proposition before the results thus educed can be regarded as trustworthy.

* "New System," i. 53. † "Ann. Philos.," xiii.

‡ See Dalton's Strictures, in his "New System," vol. ii. p. 280.

TABLE OF THE SPECIFIC HEATS OF CERTAIN BODIES, AND PRODUCT OF THEIR SPECIFIC HEAT AND ATOMIC WEIGHT.

Substance.	Specific heat.	Atomic weight.	Products.
Oxygen gas	0·2361	8	1·8888
Hydrogen gas	3·2936	1	3·2936
Nitrogen gas	0·2754	14	3·8556
Diamond	0·1469	6	0·8814
Graphite	0·2019	6	1·2114
Charcoal	0·2009	6	1·2054
———	0·2415	6	1·4490
———	0·2964	6	1·7784
Phosphorus	0·1887	31·4	5·9250
Sulphur	0·2026	16	3·2416
Selenium	0·0837	40	3·3480
Iodine	0·0541	126	6·8186
Bromine	0·1350	78·4	10·5840
Tungsten	0·0364	95	3·4580
Molybdenum	0·0722	48	3·4656
Manganese	0·1441	27·6	3·9772
Arsenic	0·0814	75·2	6·1213
Antimony	0·0508	129	6·5532
Tellurium	0·0515	64	3·2960
Bismuth	0·0308	106·4	3·2771
Zinc	0·0955	32·2	3·0751
Cadmium	0·0567	55·8	3·1639
Tin	0·0562	59	3·3158
Lead	0·0314	103·8	3·2593
Iron	0·1138	27·2	3·0954
Cobalt	0·1070	29·6	3·1672
Nickel	0·1086	29·6	3.2146
Copper	0·0951	31·8	3·0242
Mercury	0·0333	101·4	3·3766
Silver	0·0570	108.1	6·1617
Gold	0·0324	199	6·4476
Platinum	0·0324	98·7	3·1979
Palladium	0·0593	53·4	3·1666
Iridium	0·0368	98·7	3·6322

Specific Heat of Gases.—The determination of the specific heat of gases is a difficult and important problem, which has successively employed the labour and ingenuity of Crawford, Lavoisier, and De la Place, Leslie, Gay Lussac, Dalton, Delaroche and Bérard, Clement and Desormes, Delarive and Marcet, Petit and Dulong, Hermann, Avogadro, Regnault, Mayer, Böckmann, and others.

Crawford began the investigation, and, after many unsuccessful attempts, adopted the following method:—He procured two copper vessels, made extremely thin, and of the same size, shape, and weight. He filled one of these vessels with the gas under examination, previously deprived of moisture, and exhausted the other vessel by an air-pump. He next heated both vessels by plunging them into boiling water, and then suddenly immersed both in cylinders containing a quantity of cold water, the same in each, just sufficient to cover them. The vessel, containing air or any gas, raised the

temperature of the water surrounding it higher than the exhausted vessel; and, subtracting the latter increase from the former, he considered the remainder as the effect produced by the included gas, and as indicating its specific heat. The results were exhibited in a table, which it is unnecessary to insert, as they are now considered to be very remote from the truth, owing to the defects of the method of research employed by that ingenious philosopher.

Lavoisier and Laplace, pursuing the same inquiry in a different way, used their calorimeter, through which they passed a current of gas, by means of a serpentine tube, enveloped by ice. The gas was heated by passing it through another serpentine, surrounded by boiling water, before it entered the calorimeter. A thermometer, placed at each end of the serpentine of the calorimeter, measured the temperature of the gas, when it entered and when it came out of the instrument. This mode of experimenting is, however, scarcely less objectionable than that of Crawford; and the calorimeter itself has since been proved to be liable to objections as a measurer of heat, which prevent the results obtained by its means from being considered as more than loose approximations.

Mr. Leslie attempted the solution of the problem by a method founded on the following principle:—If into a large glass receiver, from which the atmospheric air has been partly exhausted, any gas be allowed to enter, the dilated air which the receiver contains will be condensed; and its temperature will be increased by a constant quantity, whatever may be the entering gas. But the gas which is admitted will absorb a part of this excess of heat, and the mixture will have a mean temperature between that of the entering gas and that which it would have acquired if it had not been obliged to part with a portion of its heat. Now it is evident that this mean temperature will be so much the lower, the greater the specific heat of the gas which enters. From experiments made in this way, the inference seemed to follow that equal volumes of hydrogen and atmospheric air have the same specific heat. Analogous experiments, however, made by Gay Lussac, gave different results. The last mentioned philosopher had recourse, therefore, to another mode of proceeding. It consisted in passing to the centre of a small reservoir, where a thermometer was placed, currents of two different gases, the one hot, the other cold. Knowing the temperature of the two gases before their mixture, and also that of the mixture, it was easy to infer the ratio of their specific heats. The numbers thus obtained do not differ very materially from those of Delaroche and Bérard.

To the last mentioned philosophers we are indebted for the joint production of an elaborate memoir, containing the results of a set of experiments made with great patience and sagacity. To their essay (published in the 85th volume of the "Ann. de Chim." and in the 2nd volume of Thomson's "Annals," 1813) is prefixed an excellent account of all that had been previously done on the same subject. They employed a calorimeter; but instead of using ice, they surrounded the serpentine tube, five feet in length, with water of a given temperature, and passed through it a known quantity of gas of a given temperature (212°) in a uniform current. The quantity of water, and the capacity of the containing vessel for heat, were previously determined; and the apparatus had the necessary appendages for ascertaining, at any moment, the quantity of heated gas passed through the calorimeter, as well as the temperature of the water. In this way each gas might be expected to impart heat to the water, in greater or less quantity, compared with other gases, and in proportion to its capacity. The following table exhibits the results of experimenters on this subject:—

SPECIFIC HEAT OF ELASTIC FLUIDS AT THE ORDINARY PRESSURE OF THE ATMOSPHERE.

	Specific heat.		Relative heat.	Authorities.
	That of water = 1.	That of air = 1.	That of air = 1.	
Air	0·2500	1·0000	1·0000	Clement and Desormes
	0·2669	——	——	Delaroche and Bérard
	0·3046	——	——	Suermann
Oxygen gas	0·1956	0·7328	0·8080	Apjohn
	0·2361	0·8848	0·9765	Delaroche and Bérard
	0·2750	0·9028	0·9954	Suermann
	——	0·9069	1·0000	Clement and Desormes, Delarive and Marcet, Haycraft, Dulong
Hydrogen gas . . .	——	9·5774	0·6640	Clement and Desormes
	3·2936	12·3401	0·9033	Delaroche and Bérard
	——	14·423	1·0000	Delarive and Marcet, Haycraft, Dulong
	6·1892	20·3191	1·3979	Suermann
	——	21·2064	1·4590	Apjohn
Chlorine gas . . .	——	0·4074	1·0000	Delarive and Marcet
Nitrogen gas . . .	0·2754	1·0318	1·0000	Delaroche and Bérard
	0·3138	1·0293	1·0043	
	——	1·0751	1·0480	Apjohn
Aqueous vapour . .	0·8470	3·1360	1·9600	Delaroche and Bérard
Carbonic oxide gas .	0·3123	1·0253	0·9925	Suermann
	——	1·0239	0·9960	Apjohn
	——	1·0802	1·0000	Delarive and Marcet, Dulong
	0·2884	1·0805	1·0340	Delaroche and Bérard
Carbonic acid gas . .	——	0·6557	1·0000	Haycraft
	0·2124	0·6925	1·0655	Suermann
	——	——	1·1750	Dulong
	——	2·7838	1·1950	Apjohn
	——	——	1·2220	Delarive and Marcet
	0·2210	0·8280	1·2583	Delaroche and Bérard
	——	0·9835	1·5000	Clement and Desormes
Sulphurous acid gas .	——	0·4507	1·0000	Delarive and Marcet
Sulphureted hydrogen	——	0·8485	1·0000	
Hydrochloric acid gas	——	0·7925	1·0000	
Nitrous oxide gas . .	——	0·6557	1·0000	
	0·2240	0·7354	1·1229	Suermann
	——	——	1·1600	Dulong
	——	0·7827	1·1930	Apjohn
	0·2369	0·8878	1·3503	Delaroche and Bérard
Nitric oxide gas . .	——	0·9616	1·7000	Delarive and Marcet
Ammoniacal gas . .	——	1·6968	1·0000	
Cyanogen gas . . .	——	0·5547	1·0000	
	——	——	1·0660	Haycraft
	——	——	1·5310	Dulong
	0·4207	1·5763	1·5530	Delaroche and Bérard
	——	——	1·5309	Delarive and Marcet

To the results of Delaroche and Bérard it has been objected by Mr. Haycraft* that they are too dependent on calculations and corrections, and that they were, in all cases, made on gases charged with moisture at an elevated temperature. He was, therefore, induced to contrive an apparatus, and to execute a set of experiments, in which these sources of fallacy should be avoided. By these he was led to conclude that all gases, simple as well as compound, have the same capacities for heat. This view, so far as respects simple gases, had already been taken by Petit and Dulong, from reasoning founded on the facts of Delaroche and Bérard; but they do not appear to have thought of extending the laws to the compound gases.

MM. Aug. Delarive and F. Marcet,† whilst admitting fully the merits of the researches of Delaroche and Bérard, are still of opinion that a few sources of fallacy were not provided against by those philosophers, which are sufficient to disturb the accuracy of their results. MM. Marcet and Delarive undertook, therefore, a new set of experiments, and extended them to fourteen different gases, all prepared with the utmost attention, and carefully deprived of hygrometric moisture. The principle of their method was, to expose equal volumes of different gases to a uniform source of heat, during the same interval of time, the volume of gas being kept uniformly the same during the experiment. By the augmentation of elastic force in each gas, they judged of the temperature which it possessed at the end of the fixed period. This was easily deduced, by means of the law which connects the elastic force with the temperature of gases. It was found that all the gases were brought to the same temperature in the same interval, proving that they have all the same specific heat, with the single exception of hydrogen gas. This gas was heated $\frac{8}{10}$ of a centigrade degree higher than other gases under the same circumstances; not, however, the authors apprehend, from any difference of capacity, but because, being a much better conductor than any of the rest, it is more quickly heated and cooled. From a review of their experiments, they consider, then, the following conclusions as legitimately deducible:—

1. That under the same pressure, and with equal and constant volumes (the elasticity alone varying), all gases have the same specific heat.

2. That, all other circumstances remaining the same, the specific heat diminishes at the same time as the pressure, and equally for all the gases, according to a progression but little convergent, and in a much less ratio than that of the pressures.

3. That each gas has a different power of conducting heat.

Such have been the principal attempts to ascertain the specific heat of different gases, attempts which may be considered as having led to no decisive results, partly from the extreme nicety and delicacy of the necessary manipulations, and partly, perhaps, from some defect in the principle of the several investigations. In cases where the quantity of matter submitted to experiment is so exceedingly minute; where the changes of temperature are so small and evanescent; and where so many causes operate, which it is difficult to separate from each other, it is not surprising that the most sagacious philosophers should have failed to arrive at sound, or even similar, conclusions. The subject then may be considered as still open to further research, and will well reward whatever skill and labour may be bestowed upon it.

The following epitome of the various means had recourse to for arriving at their results by the philosophers indicated by the preceding table, is taken from the "Handbook of Chemistry, Gmelin," English edition, vol i. p. 239:—

When the bodies of different temperatures and different capacities for heat are

* "Ann. de Chim. et de Phys." xxvi. 298. † "Ann. de Chim. et de Phys." xxxv. 5.

mixed together, the temperature of the mixture is not the mean between the temperatures of the individual subtances. Equal weights of bodies, equally heated or equally cooled, but of different capacities of heat, raise or lower the temperature of a given quantity of water through different numbers of degress, or they melt unequal quantities of ice at 0°. Spheres of equal size, and equally heated, but of substances having different capacities for heat, require different times to cool to the same point in the same medium; the radiating power of the surface being either accounted for, or made the same in all. Gases inclosed in a manometer placed in a warmer medium, require different times to produce in them the same amount of expansion by heat. The first of these methods was adopted by Wilke, Crawford, Kirwan, Dalton, and Potter; the second, by Delaroche and Bérard, Avogadro, Naumann, and Regnault; the third, particularly, by Lavoisier and Laplace, with their *calorimeter;* the fourth, by Mayer, Böckmann, Petit and Dulong, Hermann, Delarive and Marcet; the fifth, by Delarive and Marcet—for the determination of the specific heat of bodies.

After having investigated the specific heats of the different gases, MM. Delaroche and Bérard ascertained that the specific heat of any one gas, considered with respect to its volume, augments with its density, but in a proportion less than the increase of density. On this subject MM. Clement and Desormes have given the following results:—

	Under pressure of in. of merc.	Specific heat.		Under pressure of in. of merc.	Specific heat
Atmospheric air	39·6	1·215	Azotic gas .	29·84	1·000
Ditto . .	29·84	1·000	Oxygen . .	29·84	1·000
Ditto . .	14·92	0·693	Hydrogen. .	29·84	0·664
Ditto . .	7·44	0·540	Carbonic acid ·	29·84	1·500
Ditto . .	3·74	0·368			

ON ELECTRICITY.

THE science of Electricity constitutes at this time so large, and so important a branch of Natural Philosophy, that entire treatises are scarcely sufficient for its exposition. It would be impossible, therefore, in a work especially devoted to popular use, to furnish the student with more than a general summary of electrical facts and theories.

In doing this, it will be my object to direct especial attention to those points of electrical philosophy which bear more intimately than others upon its practical uses; and if the questions at issue between electricians are more summarily disposed of than their importance seems to merit, this omission is to be understood in no disrespectful sense, but in deference to the limits and the objects of this treatise; and in consideration of the existence of admirable special treatises on electricity, to which the reader who desires further information respecting the laws of that science may refer.

Definition of the Science.—The term Electricity is derived from ηλεκτρον, amber, a substance which when rubbed with silk, flannel, &c., acquires the property of attracting light bodies, which property is due to a function which philosophers have agreed to call *electricity*, and is frequently treated of as dependent on the electric fluid or fluids; although no demonstration of the existence of such fluids has ever been offered, and, indeed, the assumption of such is rather at variance than otherwise with our present ideas concerning this mysterious agency.

The attractive influence manifested by amber when rubbed, was known at very early periods, being mentioned by Theophrastus and Pliny. The commencement of electrical science, however, is of very recent date, inasmuch as this branch of philosophy is scarcely more than a century old at this time. "The philosophers of 1750," remarks Professor Delarive,* "knew very little beyond that of the nature and properties of electricity. Who at that time could have supposed that meteorology would ere long discover in electricity the cause of the grand phenomena of the atmosphere? that heat would borrow from it its most perfect instruments, and the means of manifesting its most important laws? that the molecular physics would have employed it for the purpose of penetrating into the intimate constitution of bodies; and would have caused it to concur with polarized light, in the manifestation of relations that exist between ponderable matters and imponderable ether? that chemistry would have been indebted to it for the discovery of new elements, the formation of new compounds, its most powerful means of analysis and synthesis, and the most satisfactory theories? that mineralogy and geology would, in a great measure, have found in it the explanation of the origin of their crystals and their strata? that physiology would have deduced from it a more intimate knowledge of the forces that rule over animated matter, and the secret of acting on such matter almost as life acts? that medicine would have discovered in it resources against maladies hitherto assumed to be incurable? that the metallurgic arts would have found in it new processes for extracting, moulding, and applying metals? that, finally, it would have furnished to mechanics a force as prompt as thought, equally independent of time and space—would have enabled intelligence to escape from its limited envelope to dart at pleasure with the rapidity of lightning into the most distant regions?"

* Preface to his "Treatise on Electricity."

Instead of stating the theories which, from time to time, have been adopted for the explanation of electrical phenomena, the more convenient method of study seems to be founded on a repetition of certain fundamental experiments, in accordance with which every electrical theory must necessarily be framed. The development of electrical energy from amber by friction, has already been adverted to. The next link in the chain of electrical demonstration consists in showing that the property in question is not confined to amber, but may be accepted as universal for all bodies.

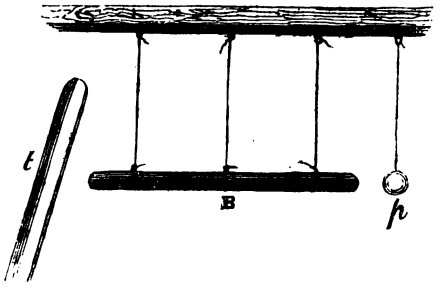
Development of Electricity.—For the purpose of this experiment the most convenient form of glass to be employed is a tube, closed at both ends hermetically, and having an external diameter of about an inch. If such a tube, perfectly dry, be rubbed with a piece of flannel, also perfectly dry, it will be found to have acquired attractive properties similar to those already referred to amber when similarly treated. For the purpose of testing the acquisition of these properties, only very simple apparatus is required. A feather, suspended by means of a silken thread (white by preference), or a light ball of elder pith, similarly suspended, constitutes a sufficient apparatus, which may be variously modified according to the ingenuity of the operator. If the glass tube, having been rubbed as described, be caused to approach the suspended feather or pith-ball, either of these light substances will be found to be affected by a certain force, appearing to emanate from the tube; in other words, the light substance will be attracted towards the tube, with which it will come into contact, and to which it will adhere if the string of suspension be sufficiently long.

For a reason to be presently explained, it will be desirable to have several feathers or pith-balls suspended, wherewith to test the electrical force of different bodies. Glass then, like amber, is capable of assuming, by friction against certain substances, the state denominated that of electrical excitement or excitation, as evidenced by its influence on a suspended light body, which evidence will henceforth be applied to determining the excitation or non-excitation of other bodies, which, when thus excited, are said to be *electrified* or *electrized*. Such electrified, electrized, or excited condition, is ordinarily spoken of as owing to the development of electricity. Extending the frictional examination to other substances besides glass and amber, the power of becoming electrically excited will soon be found to be very widely diffused. Resin, pitch, sealing-wax, caoutchouc, sulphur, gutta-percha, and generally all bodies commonly termed resinous, besides a great variety of others, will be found to acquire, after friction, the power of attracting light bodies, and hence will be said, according to a limitation of terms already accepted, to be in an electrized or electrified state. Hence, too, such bodies, very early in the history of electrical science, received the denomination of electrics.

Are all substances electrics?—To arrive at an answer to this question is very important, and, therefore, a few experiments will be indicated, from the results of which conclusions may be deduced. It will be readily seen, however, that the cause or source of electrical development with which we are now concerned—namely, ordinary friction—necessarily limits our observations to the bodies which are in the condition of solidity. If, instead of a stick of glass or sealing-wax, or, in short, any of the substances already assumed to have been employed, the experiment be varied by taking a rod of iron, brass, or any metal, not the slightest power of attraction will be evidenced on light bodies; hence this experiment, taken without limitation of others, would seem to indicate a fundamental distinction in the quality of electrical excitation for different bodies. Supposing it already agreed to term glass, and all bodies which ac-

quire the power of attraction after friction, electrics, then it would seem natural to call metals and all bodies not capable of electrical excitation under similar circumstances, *non-electrics*. Such, indeed, was a distinction long recognised; but it has no foundation in truth, as will be soon rendered apparent. If, instead of holding the metallic bar, whilst under friction, by the hand, it be held by the intervention of glass, or sealing-wax, or in short any of the substances to which the appellation electrics was formerly applied, then a totally different result will be the consequence. The metal now attracts the light body, just as glass or sealing-wax would have done; consequently it is not true to say that metals cannot be excited electrically by friction. The discrepancy must be referred to some other cause. This cause is directly related to the function explained in the next paragraph.

Can the Electrical Influence be Conveyed Away?—For the purpose of arriving at a satisfactory answer to this question, the following experiment may be performed:—



A bar of metal (B) being suspended by silk strings, and the excited glass tube (*t*) brought into contact with one extremity of this bar, the other extremity will be found to have acquired the power of attracting the pith ball (*p*) in the same manner as the tube (*t*) itself would have done; consequently, the electrical influence (whatever that influence may be) must have passed through the whole length of the metallic bar. Repeating the experiment, with the substitution of various solids for the metallic bar, the general problem, whether any solid be or be not a conductor of electricity, may be solved; subject, however, to the reservation that possibly great differences of conducting power may be regarded as absolute qualitative differences, owing to the imperfection of our experimental processes. In other words, that which is ordinarily termed electrical non-conduction may, within the limits of the experiment detailed, be nothing more than slow conduction: this, indeed, is demonstrated to be the fact. Nevertheless, the division of bodies into electrical conductors and electrical non-conductors is a good practical classification, and therefore still retained.

The appended table shows the relation subsisting, in this respect, between the bodies mentioned:—

CONDUCTING BODIES, PLACED IN THE ORDER OF THEIR CONDUCTING POWER.

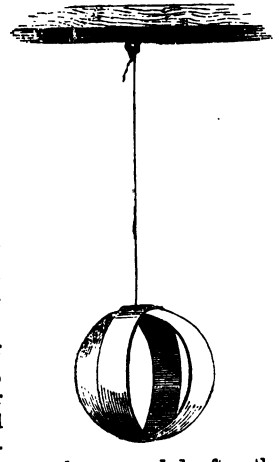
All the metals.	Spring water.	Vapour.
Well-burnt carbon.	Rain water.	Salts soluble in water.
Plumbago.	Ice above 13° Fah.	Rarefied air.
Concentrated acids.	Snow.	Vapour of alcohol.
Dilute acids.	Living vegetables.	,, of ether.
Saline solutions.	Living animals.	Earths and moist rocks.
Metallic ores.	Flame.	Powdered glass.
Animal fluids.	Smoke.	Flowers of sulphur.
Sea water.		

INSULATING BODIES, PLACED IN THE ORDER OF THEIR INSULATING FACULTY.

Dry metallic oxides.
Oils (the heaviest are the best).
Ashes of vegetable bodies.
Ashes of animal bodies.
Many dry transparent crystals.
Ice below 13° Fah.
Phosphorus.
Lime.
Dry chalk.
Native carbonate of baryta.
Lycopodium.
Caoutchouc.
Camphor.
Some silicious and argillaceous stones.
Dry marble.
Porcelain.
Dry vegetable bodies.
Wood that has been strongly heated.
Dry gases, and air.
Leather.
Parchment.
Dry paper.
Feathers.
Hair, wool.
Dyed silk.
White silk.
Raw silk.
Transparent precious stones.
The diamond.
Mica.
All vitrifactions.
Glass.
Jet.
Wax.
Sulphur.
The resins.
Amber.
Gum lac.

Gutta percha is one of the most perfect insulators, but its exact place in the above table is yet undetermined.

The reason will now be evident why brass, iron, and metallic rods generally could not manifest the power of attracting light bodies. Being good electrical conductors, the influence was no sooner developed than it passed through the whole length of the bar, through the hand and arm, finally to the earth. It is strange that so obvious an explanation of the non-excitability of electric conductors, when held immediately by the hand, was reserved for philosophers of the last few years to offer, especially seeing that electricians more than a century ago were conversant with the fact that certain bodies are conductors of electricity, and others non-conductors: indeed, without a practical application of this fact, it would have been impossible to produce artificially any electrical phenomena.



The simple experiments already given are sufficient to demonstrate two fundamental qualities of the electric influence—namely, conduction and attraction. Before, however, proceeding to another part of the investigation, it will be desirable to embody the principles already deduced in the formation of certain instruments having for their object more precise demonstrations than the simple expedients already treated of.

For the performance of class-room experiments, pith balls are inconveniently small; their place may advantageously be supplied by other simple expedients, amongst the most effective of which are the following:—

1. Two hoops may be made of thin card, or paper, and one hoop being thrust through the other, in such manner that their planes cut each other mutually at right angles, the whole may be secured from slipping by means of a little adhesive substance, or a needle-stitch; and being thus secured, may be suspended after the manner of the pith ball.

2. Instead of two hoops, one may be made considerably wider than the former, and being placed on a table, may be caused to rotate under the attraction of an excited body.

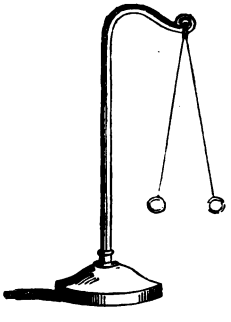
3. A very elegant means of demonstrating electric attraction on the large scale, consists of a thin bag of gold-beater's skin, or thin internal membrane of a turkey's crop, gilt.

Such are the principal instruments by which electrical attraction, and another modification of force, presently to be treated of (repulsion), can be demonstrated on the large scale. A thousand other forms will readily suggest themselves to the student; indeed, the principles of electric attraction and repulsion have been adopted in the formation of mere toys, to mention which at this time would only interfere with the sequence of deductions by which I am desirous of leading the student to an acquaintance with the laws of electrical philosophy.

Is the electric influence identical, from whatever body developed?—Whether friction be applied to glass, sealing-wax, or, in short, any possible substance, the electrical excitation resulting is found to agree in the one general respect of attracting light bodies; hence, thus far evidence seems in favour of the supposition, that, from whatever source developed, electricity is of the same quality. A few simple experiments will demonstrate, however, the fallacy of this hypothesis.

Experiment 1. Repeating the experiment with the suspended pith ball, the observer will notice that, although it be first attracted towards the excited bar, yet after coming in contact with the latter, the motive impulse is suddenly reversed, and the pith ball is repelled in such a manner that if the same excited substance be still further excited, the pith ball will, on the approach of the latter, be still more strongly repelled. Hence we arrive at the conclusion, that under certain conditions, to be hereafter scrutinized, electricity exercises a repulsive as well as an attractive force.

Experiment 2. Instead of one pith ball let two be now suspended by means of two silk filaments from any convenient support, and let any excited substance be brought near to them. Under these circumstances both the pith balls will be attracted towards the excited substance, will come in contact with it, will be repelled, and finally will repel each other, as represented in the accompanying diagram. From whatever source the electricity be developed the same result will ensue; a pair of pith balls, after being brought into contact with the excited body, will repel each other.



Experiment 3. Supposing a pair of pith balls to have been subjected to the influence of excited glass, and that they are yet divergent, let them now be touched with a piece of excited sealing-wax, or other resinous body, they will immediately tend to collapse; and if the electrical force of the excited resinous body be exactly proportioned to the force of the electricity from glass, and if the contact between the excited body and the pith balls be not prolonged for too great a period, the pith balls will remain collapsed, thus leading to the inference that the force resulting from the electricity of

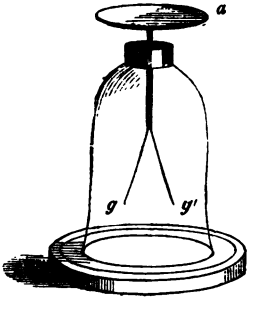
glass and vitreous bodies is opposed in such a manner to the electricity from resin and resinous bodies, that the two kinds of electricity counteract each other, and produce neutrality. Hence arises the idea of electricity as a dual force; and no theory of electricity which does not recognize this duality under some form of manifestation can satisfy the conditions which a study of electrical phenomena makes known.

Still omitting the consideration of all electrical theory, and paying attention to facts alone, as deduced from experiment, it will be now desirable to apply the knowledge already acquired to the construction of certain forms of apparatus, by means of which our sphere of information as regards electric manifestations may be enlarged.

It has been deduced from previous experiments that electricity from any one source is repulsive to itself, or, at any rate, imparts repulsive qualities to conducting bodies into the substance of which it has been conveyed. Consequently, we are furnished with a ready theoretical means of ascertaining whether the unknown electricity from a second source be similar or dissimilar to the electricity from a first or known source.

Thus, it has been already explained that the two pith balls—still divergent from the effects of electricity of glass—are caused to collapse by the influence of electricity from resin. Hence, if we denominate electricity similar to that from glass, *vitreous*, and electricity similar to that from resin, *resinous*,—then it follows that an unknown electricity which causes the collapse of two pith balls, already divergent from the effects of vitreous electricity, must be the opposite of vitreous; that is to say, must be resinous electricity, and *vice versa*. It appears, therefore, that whatever may be the cause of the duality of electric force—a duality which has been by some termed *positive* and *negative*, by others *vitreous* and *resinous*, but which, for present purposes, and to avoid theoretical considerations, may be denominated A and B—the question whether the electricity belong to A or B, may readily be determined by studying its influence on pith balls or their equivalents. This leads us to the consideration of certain important forms of electrical apparatus.

The Gold-leaf Electrometer.—This important instrument is in constant requisition by the electrical experimentalist, for the purpose of ascertaining the presence of electricity and estimating its kind. It consists of a metallic plate, *a*, communicating by a metallic stem with two sheets of leaf-gold, *g* and *g'*, inclosed in a glass vessel, for the double purpose of protecting the gold-leaf from rough mechanical injuries, and withdrawing it from the interference of atmospheric currents, which would destroy the accuracy of the results. A consideration of what has been stated in reference to the suspended pith balls, will render the nature of the gold-leaf electrometer evident. If an electrically excited body—a stick of glass or sealing-wax, for instance—be brought into contact with the metallic plate *a*, it follows that the two gold leaves *g* and *g'* must diverge; thus indicating the general presence of developed electricity. If these leaves, already divergent from the effects of a known electricity, be rendered convergent by electricity previously unknown, then this second electricity is demonstrated to be of the opposite kind to that developed from glass; is demonstrated to be electricity B, supposing that from glass to be called electricity

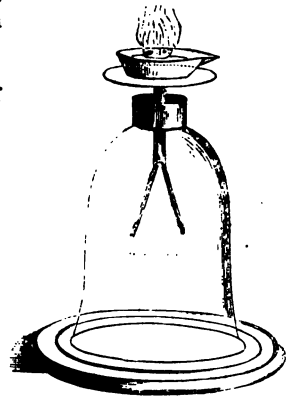


A. Hence this gold-leaf electrometer is evidently an instrument of great use in electrical determinations. This instrument was invented by Mr. Bennett; hence the name of Bennett's gold-leaf electrometer is frequently given to it. Another instrument, founded on an application of the same law, is the torsion electrometer of Coulomb. It consists of a thin needle of glass or shellac, suspended horizontally by means of a natural filament of silk as it comes from the cocoon; or by a fine metallic wire. This instrument is protected from external varying causes by insertion in a glass vessel, and the method of using it will appear from the following description:—

In the gold-leaf electrometer both leaves are free to move, and they move accordingly in obedience to the electrical force impressed. In the torsion electrometer circumstances differ: the horizontal needle of shellac, carrying at one extremity a pitch ball, is alone free to move; and the indications of the instrument are derived from noticing the extent to which the pith ball has been deflected from the conducting ball, to which the excited substance under examination has been applied. The counteracting force to electrical repulsion in the gold-leaf electrometer is gravity. Whilst electrically neutral, the gold leaves remain in close contact, on account of their own weight; but when excited they separate more or less, according as the electrical force brought into play is greater or less than their own gravitating force. Hence, *ceteris paribus*, the angle of divergence of the gold leaves should bear a constant relation to the amount of electrical force. In the torsion electrometer the counteracting force to electricity, and in terms of which the latter is measured, is torsion. The filament of silk or wire being secured at its upper extremity, this arrangement only permits the rotation of the needle of shellac by twisting. Were it absolutely unyielding, the indicating needle could not move; but yielding as it does under torsion, the force of torsion thus becomes a representative of the force of electricity; and the glass case being graduated, the angle of divergence can easily be read off. It will be seen from this description that the torsion electrometer is a more precise instrument than the gold-leaf electrometer; the latter only enabling the experimentalist to judge as to the size of the angle of divergence by rough ocular estimation. In point of fact, the term electrometer, or *electricity measurer*, in strict language only applies to the torsion instrument, the other being, more properly speaking, an electroscope; and here it may be desirable to mention, what will be demonstrated further on, that the term measurement of electricity requires limitation before it can be used with precision in the language of this science. Electricity admits of measurement as to its tension or intensity, or as to its quantity: the instruments already described only measure the former quality. The distinction between electrical intensity and quantity is one which requires to be early recognized by an inquirer in this field of science. Certain functions are distinctly referable to the first, whilst other functions are as directly referable to the second; it will be desirable, therefore, to create in the mind some palpable analogy to which these two phases of electrical manifestations may be referred. Professor Ohm has reduced the expressions to a mathematical formula, which will be given hereafter; meantime it will facilitate present investigation into the nature of electricity if the following rough analogies be adopted.

The tension or intensity of electricity may be roughly assimilated to the pressure exercised by gunpowder inflamed as a gun-charge, and the quantity of electricity to gunpowder inflamed loosely. Directing the mind into this channel of analogy, it will be seen that a given quantity, for instance twenty grains, of gunpowder rammed into a pistol would, on being inflamed, give rise to certain marked indications; there would be great pressure exerted on the internal sides of the pistol barrel; a bullet, supposing one to be superimposed on the gunpowder, would be propelled, and the act of inflammation would be accompanied by a loud sound. Here, then, is one series of effects produced by gunpowder under one set of circumstances; and the energy of these effects may be estimated in two ways. It may be estimated by noticing the distance to which a bullet is propelled by a given charge of powder; by noticing the amount of recoil, as measured by a graduated circular arc,—and in this way is the strength of a gun-charge estimated in practice. If we now suppose an equal weight of gunpowder (twenty grains) to be loosely spread over a table, and inflamed, we have no longer an indication of its force by the tests already employed. The inflammation is accompanied by no report, no palpable recoil; and if we suppose the layer of gunpowder to be indefinitely spread out, and the observer's eye to be limited to a field of vision indefinitely small, then it is possible to assume that the gunpowder might inflame unnoticed, although, by having recourse to another species of investigation, the actual quantity of gunpowder might readily be determined. This general analogy will, perhaps, aid the student in acquiring a true idea of the difference between electrical quantity and electrical intensity. The gold leaf and the torsion instrument are both restricted to affording indications of tension or intensity.

Can Electricity be developed otherwise than by friction?—By means of the two instruments already described, this point will be readily determined, and certain truths of electrical philosophy will be found to aggregate themselves into broad generalizations.



Experiment 4. Upon the plate of a gold-leaf electrometer lay a metallic capsule containing water, and into the latter drop a piece of ignited charcoal. The gold leaves will immediately diverge, proving the development of electricity. In this case there appears no doubt, on the first aspect of the case, that the electrical excitement brought about is due to the evaporation of water. By some, however, this hypothesis is rejected, and the result is attributed to chemical action ensuing between the vessel and the water, or matters contained in the water. Such an opinion is advocated by Pouillet,* who states, that if a vessel of platinum be employed (a metal on which water exerts no chemical agency), and certain precautions against error be taken, then no electrical disturbance occurs. The objection thus raised is most important, as between the questions whether evaporation, *per se*, be a source of electricity, or the contrary; but it has no bearing upon the question at this time proposed for determination. Whatever may be the source of electricity in this case, friction assuredly

* "Ann. de Chim. et de Phys.," xxxv. 401; and xxxvi. 5.

is not; and this alone is sought to be determined by the experiment under consideration.

Perhaps no experiment so unequivocal as that just described could be performed with the same object in view. The general demonstration of the proposition that friction is not the only cause of electrical excitement, is sufficiently easy; but when investigation is made as to the exact nature of the non-frictional excitements, then difficulties present themselves which no ingenuity has yet been able to master, and which prevent our arriving at certain determinations relative to important primary laws. Thus, for instance, it will be seen hereafter, that philosophers were long undetermined as to the primary cause of electrical development from voltaic arrangements; indeed, it would be, perhaps, scarcely correct to say that the question is resolved definitively, even at the present time. The question at issue was, whether certain dissimilar metals—especially zinc and copper—do or do not suffer mutual electric disturbance when brought into contact. Apparently, nothing is more easy than the solution of this question. The gold-leaf electrometer would seem to furnish us with the means; but the difficulty which cannot be overcome is this: the impossibility of bringing into contact, and separating two metals, without exercising a certain amount of friction. These remarks are offered for the purpose of showing the extreme delicacy necessary in conducting electrical experiments, the difficulties with which these experiments are beset, and the care with which incorrect deductions should be guarded against.

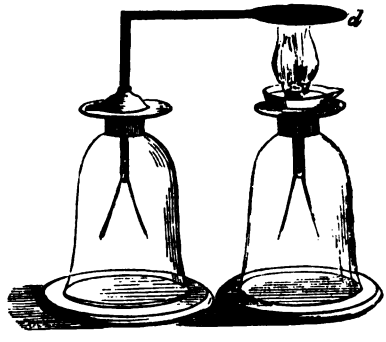
Can one kind of Electricity be developed without the other?—Hitherto, for the sake of simplicity, it has been assumed that only one body in each experiment has been subjected to the preliminary treatment to which electrical excitation is referable. A slight amount of reflection, however, will show this assumption to be incorrect. In all the experiments detailed there has been a duality of preliminary agency. Thus, if a glass tube be submitted to friction, then, strictly speaking, two substances are rubbed, not one; moreover, the distinction between the rubber and the substance rubbed is merely conventional. In strict philosophical language both are equally rubbed; consequently, if it be desired to recognise the total consequences of such friction, not only must the glass tube be submitted to examination, but the flannel or silk wherewith friction was exercised.

Supposing it be desired to ascertain the presence of electricity on the rubber, to use a conventional term, as well as on the material rubbed, some precautions, easily deducible from previous considerations, will be necessary. The question, however, may be resolved as follows:—Let a cylindrical portion of flannel, *f*, be adapted to the glass tube *t*, as represented in the woodcut; and, in order to restrict the area of friction within definite limits, let the glass be rotated instead of moved forwards and backwards. If the glass tube thus rubbed be caused to approach a gold-leaf electrometer, the leaves will diverge, as we have seen. If now, instead of one electrometer, we employ two—one for testing the glass, the second for testing the flannel—then divergence of the gold leaves of the second instrument will also result, proving that both glass and flannel have been electrically excited. It remains, therefore, to determine whether they have been excited by similar or different kinds of electricity. Now it has been already demonstrated that the two kinds of electricity are mutually attractive and mutually neutralizing; consequently, if two bodies be electrically excited,

one giving rise to a repulsion between two light substances—which repulsion the other neutralizes—the second body is differently electrified to the first. Supposing, therefore, the two electroscopes to be still divergent, and the frictional operation repeated,—if the flannel be now caused to touch the instrument formerly touched by the glass, and *vice versa*, the gold leaf of both instruments will immediately collapse.

These experiments show that, in the case under examination, one kind of electricity cannot be developed without the other; and the same may be easily proved, for every case of frictional excitement may be extended experimentally over a vast field of inquiry, and carried further by analogical reasoning, so as to satisfy all cases of electrical relation whatever. The proposition of double development is easily proved for the case of evaporation, already cited, in the following manner:—

Let the vapour arising from the evaporating water be made to impinge against a metallic disc, *d*, situated above it, and communicating by a bent metallic stem, ending in a metallic foot, with the plate of a second gold-leaf electrometer. Matters being thus adjusted, the gold leaf of both electrometers will be found to diverge; and now, on establishing a metallic connection between the two plates of the electrometers, both pairs of gold leaf will immediately collapse, showing that the electricities are of different kinds. The experiment proves something more, which will be specially demonstrated in the next paragraph. Perhaps it is unnecessary to point out, that in establishing metallic connection between the two electrometer plates, it is necessary that the metallic conductor should be "insulated," as the condition is termed by electricians; that is to say, it should be held not immediately by the hand, which is an electrical conductor, but by the intermediation of a non-conducting material, such as glass, shellac, sealing-wax, &c.

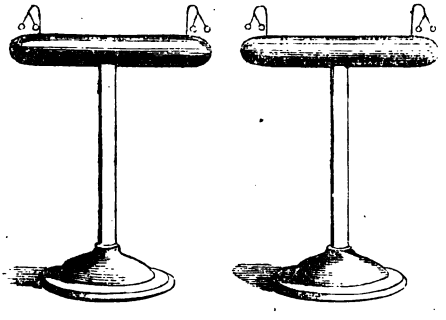


Are the Electricities developed proportional, or is one kind ever in excess?—This question has already been resolved, for one specific case, by the last experiment; the following method, however, will render the demonstration still more clear. Taking the glass tube with its cylindrical flannel rubber, as already described, let friction be exercised as before; then let both flannel and rubber be brought in contact with the plate of a gold-leaf electrometer. Not the slightest divergence will take place, if care have been taken not to extend the frictional area beyond the edges of the flannel cylinder. This experiment proves, for the case under consideration, that the two kinds of electricity are developed in exact proportion; and the same may be demonstrated for all kinds of electrical excitation whatever. A deeper consideration of the truth embodied in the proposition that the two kinds of electrical force are mutually proportional, leads to the most subtle branch of electrical philosophy—the so-called state of electrical induction; the nature of which will, it is trusted, be rendered evident by the course of investigation about to be adopted. It has been said that one kind of electricity cannot be alone developed, *neither can it exist alone when developed*—a remembrance of which proposition will remove the difficulties attendant upon a just comprehension of what is called the *induced electricity*.

But if electricity cannot exist alone, what explanation is to be given of the following experiment? A metallic ball, insulated by means of a silk cord, is touched several times in succession by a piece of glass, electrically excited. Under these circumstances the metallic ball becomes charged with the electricity of glass, as may be demonstrated by bringing into contact with it a little disc of gilt paper—also insulated—removing the plane by means of its insulating stand, and bringing it into contact with the plate of an electrometer. The gold leaves instantly diverge, proving the accumulation of electricity in the metallic ball.

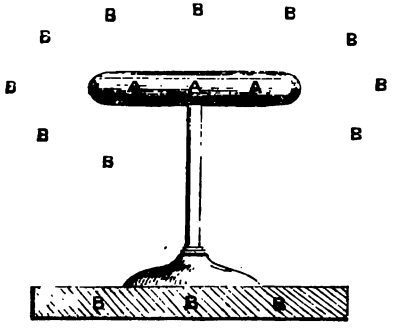
How can it be said, then, that one kind of electricity is incapable of a separate existence? Is not the metallic ball electrified? On this point it is desirable to have the most precise notions, otherwise the so-called function of electrical induction will lead hereafter to interminable difficulties.

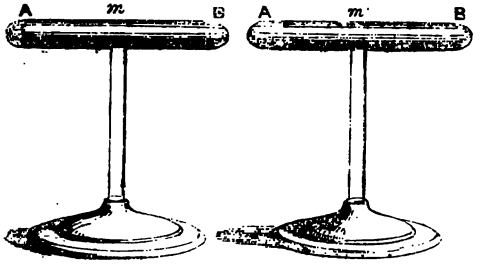
The fallacy in which the inquirer is likely to be involved when contemplating the bearings of this experiment, results from considering the metallic ball as isolated in every sense from surrounding bodies. Such isolation, however, is impossible, not only when practically considered, but theoretically also. Even were it self-supported, without any aid of the cord, it would not be isolated. Even if the air were removed, it would not be isolated. Even if our globe, atmosphere, and all were annihilated, and the brass ball left a minute asteroid in its place, the ball would still not be isolated, for it would still maintain relations with other masses in space. In contemplating, therefore, the condition of the suspended brass ball, it must be regarded in relation to surrounding matter. The necessity for a dual investigation is equally great in this case, as when it was proposed to examine the electrical disturbance resulting from the friction of glass and flannel. Before the proposition can be accepted, that one kind of electricity exists in the metallic ball alone, it will be necessary to examine the condition of the atmosphere around the objects in the vicinity, not forgetting to enumerate amongst the latter, the operator himself. If this investigation be carried out, the general proposition will be found to hold good, that the suspended metallic ball has disturbed the electric equilibrium of surrounding bodies to a state proportionate with its own degree of excitation; and the electrical charge which the metallic ball can retain will *ceteris paribus* be proportionate to the nature and the number of material particles in its vicinity. To render this proposition more evident, two metallic balls may now be suspended, or, better still, for reasons which will appear hereafter, two metallic cylinders, with spheroidal ends, as represented in the accompanying diagram. The cylinders may be suspended, each by two silken threads, or, what is still more convenient in practice, they may be supported each on a glass stand; and for the purpose of indicating the presence of electricity, each cylinder may be supplied with two pairs of pith balls, one for either end, and attached as represented in the diagram. The strings by which the pith balls are suspended in this case must be of thread, or other conducting material, because it is desired that electricity should



pass along them. Provided the two cylinders are separated from each other to a proper extent, which practice alone can determine, the following result will occur:—On directly electrifying one of the cylinders by contact, the other will become electrified also, as indicated by the divergence of the attached pith balls.

At first it might be inferred that direct transference of electricity from one cylinder to the other had taken place; but this idea is readily disproved by removing the second cylinder, when the pith balls attached to it will at once collapse. To what then was the electrical excitation attributable which it manifested whilst standing near the adjacent cylinder? The excitation is attributable to the exercise of a function already conveyed in the proposition just laid down. The first cylinder is only able to maintain its electricity, A, by developing a proportionate amount of electricity, B, in adjacent bodies. So long as the cylinder was alone, the second, or B, function of electric duality was scattered, to use the expression, indefinitely around (it is represented by the diagram affecting the air and the table); but immediately a second cylinder was placed near, the A and B powers of electricity became distributed, as represented in the accompanying diagram.

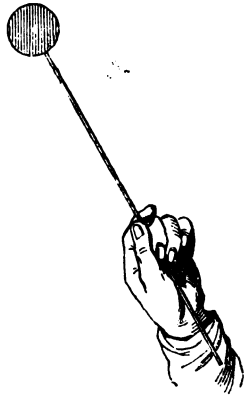


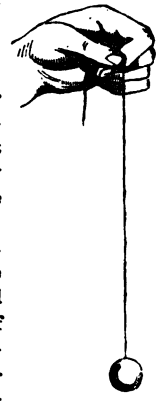


That such an arrangement of electrical force really takes place may be demonstrated by a very simple experiment. If the proposition just laid down be true, there should exist a mesial line, *m m'*, in each cylinder, devoid of all electrical power. That such really is the case may be demonstrated by fixing a pair of pith balls at this line, under which circumstance no repulsion of the balls should take place, if the exact mesial line be selected. In practice, this exact selection is scarcely possible; nevertheless, a sufficiently near approximation may be arrived at to demonstrate the general soundness of the law. Moreover, it may be further demonstrated that in the two cylinders placed as described, the A function and the B function of electricity are distributed, as represented in the diagram, by means of an insulated carrier plane of gilt paper and a delicate electrometer. The terms carrier plane and carrier ball will be frequently employed. A carrier plane consists of a gilt-paper circular disc, about two inches in diameter, insulated by a band of shellac; a carrier ball is a ball of brass or other metal, suspended by a silken string. (See two diagrams on next page).

It is evident that any conventional sign may be employed in the designation of the two electrical functions. I have taken the letters A and B. Instead of these letters, the plus and minus, algebraic signs (+) and (—), are generally employed, and I

have merely avoided them because of their association with a particular electrical theory—namely, that of Franklin, according to which it is assumed that the two electric functions stand to each other in a relation parallel to heat with cold; that is to say, that one is a mere condition of absence of the other.

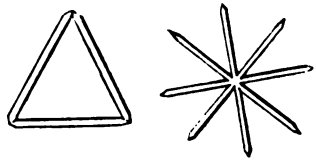




Electrical Inductions.—Under this denomination was formerly expressed the state of electrical excitement developed in one body by proximity with another, as we have seen in the previous experiment; and the term, electricity by induction, or induced electricity, was employed so as to imply the supposition which was indeed intended to be conveyed, that the function of induction might or might not be co-existent with a primary electrical excitement. It has been the object of preceding remarks to show that it necessarily must be co-existent with electrical excitement, of which, indeed, it forms a part. For this important generalization we are indebted to the investigations of Faraday, who has laboured so long and so successfully in this interesting field of inquiry. It appears, therefore, that the term electrical induction, in a partitive sense, is no longer intelligible; nevertheless it has been so long accepted, and has become so intimately associated with the explanation of many important electrical phenomena, that, limited according to previous explanations, it will hereafter be employed in this volume.

What is the condition of the atmosphere, or other non-conducting medium, through which the inductive influence takes place?—It has been demonstrated in the preceding pages, that an influence, or force, has in some way been exerted through the layer of atmospheric air situated between the two cylinders which formed the subject of experiment. A question, therefore, at once presents itself of the following kind. How is the atmosphere itself affected by the influence transmitted through it? Is the atmosphere passive or active? Anterior to the investigations of Faraday, it was usual to answer the second question in the negative; the influence, whatever it may be, was assumed to radiate or pass in straight lines through the atmosphere, which itself remained passive, being nowise affected. Faraday has demonstrated the incorrectness of this theory; he has shown that the atmospheric molecules assume a polar state, and to this polar influence is attributable the electric manifestations recognizable on the second cylinder, or any other conducting body similarly circumstanced. The term polarity is one so frequently employed in the description of molecular forces, that it is necessary at this point to describe its meaning. By the term polarity is understood a certain symmetry of relation subsisting between the components of a material aggregate. Thus, for instance, supposing the aggregate to consist of a heap of needles confusedly arranged, then the components of this aggregate (*i. e.* the needles) would be said to manifest no polarity. If, however, the needles were to form any symmetrical groups, such as stars, triangles, &c., then the aggregate of needles would be said to have become endowed with polarity; the formation of such aggregates

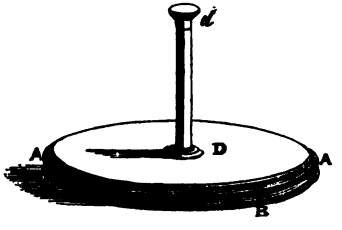
would be expressed as the assumption of polarity, and the destruction of the symmetrical groups as the resolution of polarity. The idea thus grossly expressed evidently admits of extension to the smallest molecules, or even to the forces actuating these molecules, and the assumed polar state of molecules and forces may be rendered comprehensible generally by gross physical analogies. Reverting to the foregoing experiment, it will be seen that the cylinders operated upon are affected by polarity, the ends A being in symmetrical relation to the ends B; and their length might be indefinitely extended with a similar result.



Mr. Faraday believes that atmospheric air, or other non-conducting material, interposed between the two cylinders, or any bodies similarly circumstanced, is not passive, but active — that the influence, by means of which the first cylinder is enabled to affect the second, is not darted through the intervening space by a sort of radiation, but that the atmospheric molecules assume some sort of symmetrical relation, either of form or of force, which symmetry of relation extending in all directions, not merely in straight lines, from the primarily electrified body, affects directly, but in a manner unknown, the second.

To inquire more narrowly into the nature of this transmitted power is equivalent to the inquiry, *What is the nature of electricity?* Hereafter a short exposition of the various opinions relative to this question will be given; but to enter into the speculation at this time would carry us too far from the sphere of present discussion.

The Electrophorus.—Accepting the term electric induction with the limitation already stated, I shall now describe an instrument which not only illustrates that function, but which is an instrument of great practical utility. The electrophorus, as it is called, was the invention of Volta, and is thus prepared:—Procure a flat dish of metal, B (tin plate, copper, or brass) about one inch deep and twelve or fifteen in diameter; fill this dish with a resinous mixture of equal parts of shellac, resin, and Venice turpentine, and allow the whole to grow cold. One half of the instrument—to which the term "*sole*" has been given—is now prepared, and it only remains to form the cover. This consists of a thin, flat, metallic plate, D, something less in diameter than that of the sole, and furnished with a round band, or metallic rim, as shown in the diagram, A A. To this cover a glass handle, *d*, is attached by means of a socket, into which is run a little cement.



When it is desired to bring the electrophorus into action, the sole, or resinous face, is briskly rubbed, or rather *dashed*—the operation being something between a blow and a rub—with a piece of dry flannel or fur-skin. This operation having been repeated five or six times in succession, the excitation is complete. The whole upper surface of the sole is now affected with resinous electricity; and if the cover fitted it accurately at every point, the resinous electricity thus developed would be communicated to the cover by simple contact. This condition, however, never obtains. The cover does not actually touch the resinous portion at more than a few points, from which resinous

electricity is directly transferred. The greater portion of the surface of the cover, however, is separted from the resinous face of the sole by a thin layer of atmospheric air; consequently it is placed under the conditions most favourable to the assumption of electricity by induction. The method, then, of employing the electrophorus is as follows:—The cover being laid upon the resinous face, which is resinously electrified, the lower aspect of the cover at once becomes vitreously electrified, and its upper aspect resinously; if, however, the cover be touched with the finger, or any other conductor in communication with the earth, then the binary system (namely, the sole and the cover) becomes neutral. This neutrality, however, exists only so long as the two binary portions of the instrument are in close relation. If the cover be removed beyond the influence of the sole, then the balance of electrical neutrality is destroyed, and the cover becomes charged with an excess of vitreous electricity, which it will evolve in the form of a spark, on causing it to be approached with a metallic knob, the finger-knuckle, or any other non-pointed conductor.

The Condenser.—The law of electric induction is beautifully illustrated by the condenser, an instrument designed to manifest very slight amounts of electrical influence, such as would not be rendered evident by the unaided electrometer.

The condenser is represented by Fig. 1. It consists of two circular metallic discs, one, B, insulated on a glass stand, and a fixture; the other attached to a metallic stem, which inferiorly terminates in a pivot, so that the plate of the instrument marked A, although represented vertical in the sketch, may be turned back at an angle, and laid horizontally if desired. Occasionally, instead of attaching this plate by means of a hinge, it is fixed to a slide, which enables it to be removed from the plate B, still retaining its vertical plane.

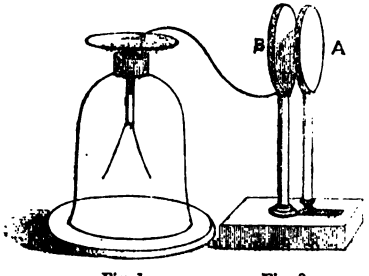


Fig. 1.

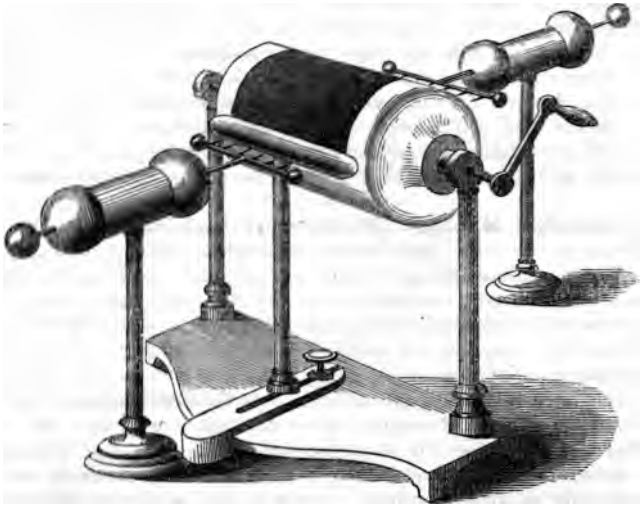
Fig. 2.

In order to understand the theory of the condenser, the most convenient plan is to impress the mind with the result that would take place on one insulated disc when touched with an electrically excited body. From what has been already stated, it will be evident that the total amount or charge of electricity capable of being received by such a disc, will depend on the amount of opposite polar influence capable of existing in bodies around or near it; and if a conductor should happen to be in its vicinity, this disc should receive a stronger charge than if such conductor were away. The second plate of the condenser, therefore, supplies this definite theoretical indication, and enables the first plate to acquire more electricity than it otherwise would. Still, while the plates are opposed to each other, no electrical influence is manifested; the two systems being mutually balanced. But immediately one plate is removed, then the remaining plate contains an overcharge of electricity, which it can impart to any other conductor by simple contact. The diagram represents the condenser, united by a conducting wire with a gold-leaf electrometer in the act of divergence. Strictly speaking, however, the divergence would only have occurred when the plate A of the condenser had been withdrawn.

The method of using the condenser will be evident from a consideration of the principles on which it is based. The two plates being placed in opposition (not in contact), plate B is touched with the substance whose electricity is to be examined, and A is simultaneously touched with the finger or a conductor, if it do not happen to be mounted on a conducting stom. This process being several times repeated, the binary system becomes fully charged, and accurately balanced—the electricity of one disc against that of the other. Immediately, however, disc A is removed, then the original balance between the two systems is destroyed, B has a surcharge of electricity, which it transmits to the electrometer leaves, and thus causes them to diverge.

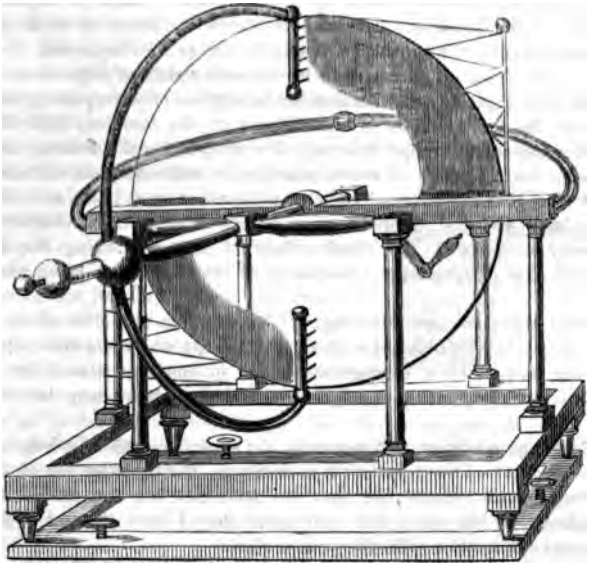
The Electrical Machine.—Hitherto in our development of the laws of electrical phenomena, the very simplest means of electrical excitation were adopted. It would be possible, without having recourse to more complex apparatus, to push our investigations still further; nevertheless they will be greatly facilitated by no longer trusting to the minute quantities of electricity already developed, and employing the electrical machine, a description of which I will now proceed to give. The term electrical machine, it should be premised, is limited to include those instruments merely which yield electricity by frictional excitation. In the strict language of philosophy, Voltaic batteries are electrical machines, as are also those combinations now so prevalent by means of which electricity is developed from magnets. None of these instruments, however, are usually termed electrical machines. The electrical machine, in its most generally received acceptation, consists in some mechanical arrangement for extending and enlarging the frictional efforts already described, and conducting and retaining the resulting power. It admits of various modifications as to form, but the philosophical principles on which it is founded never vary. An electrical machine consists of three main portions, namely, the rubber, or friction giver; the electric surface, or friction receiver; and the prime conductor. The very oldest electrical machines had their electric surface constituted by a glass globe, and the rubbing apparatus was flannel, or other material held in the hand. Subsequently glass globes were found to be inconvenient in practice, and cylinders were mounted in their stead, the friction-giving portion of the machine being no longer held in the hand, but made a fixture. Occasionally the prime conductor was also fixed in the early electric machines, but more frequently detached. At present the electric surface is more usually made in the form of a plate than cylindrical, many practical difficulties occurring to prevent the formation of cylinders of large size. Whether a flat plate or a cylinder, however, the general principles on which the construction of an electrical machine is based are not affected, as will be easily recognised. In all electrical machines, the prime conductor, or instrument which conveys away the electricity from the electric surface, is insulated by glass—the reason of which provision will be obvious from a consideration of what has gone before.

In cylindrical machines the rubber is also insulated, conduction being established, when necessary, between it and the ground, by interposing a metallic chain. The contrivance of insulating the rubber affords certain facilities in the production of resinous, or *negative* electricity, as we may now call it, under the limitation already given; but it is a provision rather difficult of execution in plate machines, and is, therefore, in the latter frequently omitted. Occasionally, when the rubber is insulated, it is attached to a prime conductor of its own. The following woodcuts represent a cylindrical and a plate machine respectively.



Action of the Electrical Machine.—It has already been demonstrated, that when a rod of glass is rubbed by means of a piece of flannel, the glass itself becomes electrified in one state, and the flannel in the other. These facts being appreciated, the action of the electric machine will be evident. Regarding the various portions of the machine as one electric system, each part cut off by means of insulating legs from all electric communication with the ground, then the total accumulation of electricity in the prime or positive conductor, or that to which the rubber is not attached, will be limited to the total amount of positive electricity originally existing in the system, and will be exactly balanced by the amount of negative electricity originally existing in the system, and which is now determined towards the rubber. Under these circumstances the tension or tendency of the electricity accumulated at the prime conductor will be very slight. If, however, metallic communication be established between the rubber and the ground, then the tendency of the prime conductor to evolve electricity will be in the direct ratio of its own surface to that of the whole surface of the earth. This ratio, it will be seen, is practically infinite; therefore electricity will be now evolved from the prime conductor so continuously, that it is somewhat difficult to prevent the mind associating itself with the idea of a real electric current: although, in point of fact, this seeming current is probably nothing more than a series of rapidly-occurring polarities, assumed and immediately resolved.

Management of the Electrical Machine.—The two chief points to be attended to in the management of apparatus connected with the development and preservation of frictional electricity are absolute cleanliness and absolute dryness. Any flagrant violation of either of these conditions will be found incompatible with the successful performance of electrical experiments. The necessity for perfect dryness naturally suggests the avoidance of water in the cleansing operation; hence alcohol or oil is



substituted in its place. The frictional surface of the machine, whether a plate or cylinder, should be carefully examined for all specks, stains, and other impurities, which being removed, so far as they permit, by the exercise of mere rubbing with a piece of chamois leather or silk, any remaining portion should be moistened with olive oil, loosened by renewed friction; finally, the oil should in its turn be wiped off, and the glass, if not perfectly clean, moistened with alcohol, and rubbed until dry.

As regards the rubber portion of the machine, it does not consist of a simple pad, but the surface of the pad is smeared with an amalgam of tin, zinc, and mercury—a mixture which is found to conduce to electrical development; but as this compound soils the glass portion of the machine, the latter requires to be cleansed from adhering streaks of dirt more frequently than it otherwise would.

The next point for consideration is the composition and formation of the amalgam, also the method of laying it upon the surface of the rubber.

The amalgam itself is formed of tin, zinc, and mercury, equal parts of each. The two former are fused together in an iron ladle, the mercury added, rapidly incorporated, at once removed from the fire, thrown into a wooden box containing powdered chalk, and agitated until cold. It is now transferred to a mortar, all inequalities broken down with the pestle, and incorporated with about one-eighth of its own bulk of pomatum. The amalgam, thus prepared, may be squeezed into a mass and smeared over the surface of the rubber.

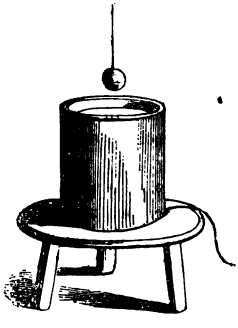
When electrical experiments are carried on in an airy, well-ventilated room, when

the weather is moderately dry, and the individuals present are but few, there is no great difficulty experienced in preventing the deposition of aqueous vapour upon the various parts of the machine. The case is otherwise, however, when prosecuting electrical experiments in a crowded apartment, such as a lecture room. Under these circumstances, much care is necessary to insure such a state of dryness as may not be incompatible with experiments. Perhaps the best means of accomplishing this consists in placing on the lecture-table, in the vicinity of the machine, little furnaces or chafing-dishes containing ignited charcoal. For the purpose of increasing the radiating or heat-giving surface, discs of metal, circular by preference, should also be supported over the glowing charcoal by any adequate means. Gas and oil lights do not answer well the end desired. A main result of their combustion is water, which greatly counteracts the direct effects of heat. Burning charcoal is not attended with this disadvantage; the result of its combustion being carbonic acid alone.

As regards the glass insulating legs of the machine, it is difficult to keep them quite dry, except they be overlaid with varnish. That which answers most satisfactorily for the purpose is a solution of shellac in spirit of wine. By the aid of the electrical machine, our knowledge of electrical agencies may be now further extended.

Does Electricity, whilst at rest, penetrate the whole substance of a body, or is it confined to the surface?—The experiments necessary to the investigation of this subject admit of performance without the electrical machine; but they are so much more readily conducted by the aid of that instrument, that I have thought it desirable to postpone their consideration until the present time.

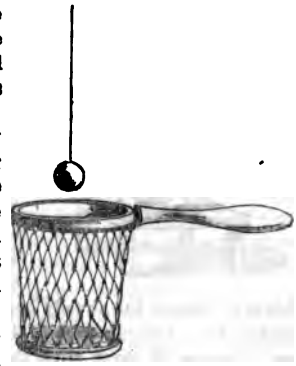
If any hollow vessel of conducting material be taken (an ice-pail answers perfectly well, placed upon a stool having glass legs, and hence commonly known as the insulating stool), an electrified body brought into contact with the hollow vessel necessarily conveys electricity to the latter. In conducting this experiment, the electricity may be taken from the prime conductor of an electrical machine by direct metallic contact with the latter, and a carrier-ball of metal, insulated by attachment to a silk cord, may be employed to convey away the electricity from the charged vessel to the testing electrometer.



Arrangements being thus made, if the carrier-ball be brought into contact with the external surface of the vessel, then removed and caused to approach the plate of a delicate electrometer, the gold leaves will instantly diverge, thus proving the existence of electricity. If, however, the carrier-ball be now dipped within the vessel, brought into contact with its inner surface, and again brought into contact with the electrometer plate, not the slightest divergence will ensue; thus proving that the electric influence is totally confined to the external portion of the vessel. Nor is the general result altered if, instead of a vessel having solid sides, one having orifices be substituted—such as a mesh-work cage of wire gauze. But perhaps the most striking form of conducting the experiment is as follows:—

The annexed vessel represents an instrument composed of an insulating glass

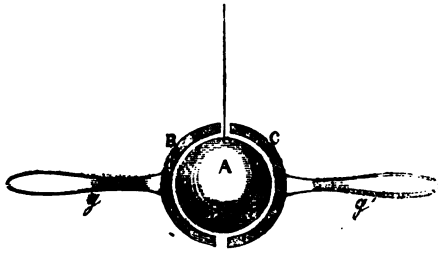
handle and a brass ring,—a heavy brass bottom, the latter suspended to the ring by means of network of linen, not silk, threads. A network of metallic wire would have better fulfilled one condition of the experiment; but it would have necessarily been rigid, and consequently unadapted to the mechanical necessities of the instrument, as will presently appear.



The object of this contrivance is as follows:—By means of dexterous manipulation it admits of being turned inside out without touching; so that the internal portion of the net may be made at pleasure the external portion, and *vice versa*. If the insulated carrier-ball be dropped inside this network, brought in contact with the metallic bottom, removed and tested by means of a gold-leaf or torsion electrometer, not the slightest electrical excitation will be manifested; whereas, by reversing the conditions, ample proof of electricity will result.

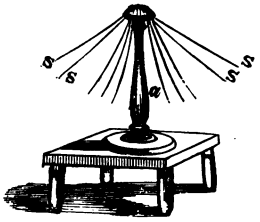
Perhaps no devices can more strikingly illustrate the proposition that electricity, whilst at rest, occupies the surface of bodies, than these already cited; the following, however, being easy of execution, may be stated.

Let A be an insulated metallic ball, charged with electricity, and B C metallic hemispherical cups, which being approximated, by means of their insulating glass handles *g* and *g'*, embrace the ball. Under these circumstances the charged ball will be found, if inclosed within its metallic hemispheres for an instant and the cups removed, to have lost all its electricity. Another form of demonstration is as follows:—S is a sheet of thin metallic foil, wound round a cylinder, *c*, which latter is insulated. Attached to the cylinder, by metallic communication, are two pith balls, which serve the purpose of an electroscope. By turning the cylinder on its axis the metallic foil will be wound up, its surface being lessened, although its metallic mass remain the same. Under these circumstances the pith balls will diverge, indicative of an increased tension or accumulation of electricity on a limited area. This experiment is the more striking that it does not require electricity to be imparted from any extraneous source; the electricity naturally existing in the metallic leaf being that which is called into active play.

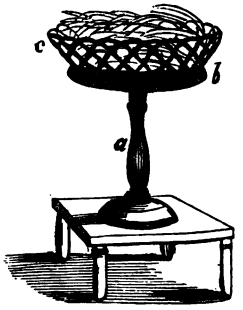


The preceding experiments are direct; but the proposition may be demonstrated indirectly, by experiments which have already been mentioned with a different object. The

mutual repulsion of light bodies, when duly considered, is another proof that electricity resides on outside surfaces, and that in endeavouring to get as far as possible away, it carries with it the light bodies themselves; the demonstration, however, is rendered more striking by employing an instrument of this kind:—*a* is a vertical stem of conducting material, insulated by placing it on a glass-legged stool; *s s s s*, &c., are strips of paper attached to its upper extremity. When the stem *a*, and, consequently, the strips of paper, *s s s s*, are brought into communication with the charged prime conductor of an electrical machine, a mutual separation of the strips of paper takes place. They are not, however, equally separated throughout their whole depth. The outside ones separate first; and when they are sufficiently removed from the central influence, others follow. Now it has already been demonstrated that bodies similarly electrified repel each other; consequently, if the electricity were equally distributed throughout the entire layers of paper slips, they should undergo mutual repulsion throughout their entire depth.



The following experiment, again, illustrates the same proposition; and it will be found to have a double significance:—*a* is an insulated conducting stem, terminated by a metallic platform, *b*; *c* is a little basket, or any other vessel of conducting material, possessing a similar depth and general shape. The basket contains shreds of tissue-paper, each about an inch square. If the basket and its contents be now brought in communication with the prime conductor of an electrical machine, and if the prime conductor be very gradually charged, a portion of the paper shreds may perhaps be repelled, and fly out of the basket. Whether, however, this result takes place or not depends entirely on the depth of the basket; and by supplying a basket of sufficient depth, the mutual repulsion of the paper slips may be altogether prevented. Instead now of exposing the paper slips in a basket to electrical influence, place them on the metallic disc *b*, and bring the apparatus in communication with the prime conductor of an electrical machine as before. Mutual repulsion between the paper cuttings now takes place; they rise out of the basket, extend outwards, and ultimately fall. Thus it is recognised that the act of mutual repulsion is dependent on the depth of the basket—on the amount of *outsidedness*, to use an allowable expression, possessed by the apparatus.



But the experiment has another significance: the paper shreds are not scattered at once throughout their whole depth, as they would have been by the exercise of a homogeneous repulsive force, but the outside pieces are first repelled, then follows another layer, then the next, and so on to the end. A consideration of this tendency of electricity to approach the outside of conducting bodies is one which has numerous practical bearings, and merits a still more attentive consideration than has already been given to it. The theory of lightning-conductors, for instance, mainly depends upon it, as will soon be manifest.

Outsidedness of Electricity Proved.—Starting from the original proposition, that electricity is alone confined to the outside of bodies, it will now be desirable to trace its relation to conductors of various shapes; and here I shall have occasion to employ a term already adopted—*outsidedness*. A slight consideration of various mathematical solids will demonstrate that each solid possesses an amount of outsidedness peculiar to itself; understanding by that term the mutual distance of points on the surface of each solid from the latter's centre. It will be evident that a sphere will have this outsidedness more equally diffused than any other form whatever; and that a point will depart to the farthest extent possible from this condition. It follows, therefore, that electricity should be most equably diffused over the surface of a sphere; and in proportion as the conductor assumes the pointed form, so will the electric inequality be greatest. Experiment bears out the supposition most remarkably. If a spherical insulated conductor be brought into communication with the machine, and sparks drawn from the sphere by approaching it with a metallic knob, it will be found that on all aspects of the spherical conductor, sparks of equal size—in other words, of equal character or power—may be drawn. Immediately, however, that the spherical form is departed from, a different result is obtained. Taking a cylinder, for instance, it will be found that a spark drawn from either extremity differs in quality from the spark drawn from either side; and, in short, without needlessly multiplying further examples, a similar progression of results will be made evident as the experimenter proceeds from the spherical to the pointed type. At length, when arrived at the pointed form, the experimenter will discover that the electrical condensation tension, or, to adopt the language of theory, electrical pressure, is so great, that no spark whatever can be drawn from the point from which the electricity escapes in a continuous stream. To demonstrate this proposition nothing more is required than the attachment of a needle to a prime conductor in such a manner that the point of the needle looks outward. Under this arrangement it will be impossible to retain electricity on the prime conductor; and if the experiment be performed in a darkened room, the escape of electricity will be rendered manifest by the appearance of a luminous object known as the electric pencil or brush.

The preceding experiment has been described, for the sake of simplicity, as though the passage of electricity had reference to the prime conductor of the machine alone, considered as an electric source; but it will be obvious, from a proper application of the theory of induction already explained, that the machine prime conductor can only be regarded as the representative of one member of a duality, the second member of which is the whole earth. In other words, regarding the prime conductor of an electrical machine as electrified + or plus, this electricity must be balanced by its counterpart of — or minus electricity existing on some other body; which body, provided no amount of insulation take place, is the whole earth. Whence it follows that all which has been stated in reference to the giving out of electricity by the prime conductor, or conductors, of various shapes, brought into electric communication with it, apply conversely to a reversal of the arrangements already detailed; or, to be practical, if a needle attached to the machine prime conductor be potent in giving out electricity to the earth prime conductor—so conversely a needle attached to the earth prime conductor—(*i. e.*, held in the operator's hand), will be equally potent in receiving electricity from the prime conductor from the machine; and generally the proposition in its widest significance may be thus embodied: *The capability of any mechanical form for giving electricity is equal to its capability for receiving it.*

Thus the general proposition is demonstrated that electricity resides on the surface of bodies, not penetrating to any sensible depth; hence the capacity for electricity—to use a figurative term—will, *ceteris paribus*, be proportionate to the area of surface. It must be pointedly inculcated, however, that this remark only applies to electricity in a static or motionless condition. Where electric currents are concerned, the power of a conductor to transmit a given charge is proportionate to the mass of conductor of equal conducting power. This is a circumstance of great practical importance; on its comprehension is based the construction of lightning rods; experience having determined that for each conducting body there exists a solid transverse section, competent to give ready passage to the largest known discharge of atmospheric electricity. The following numbers represent the facility with which different metals conduct electricity:—

Silver	136
Gold	103
Copper	100
Zinc	28
Platinum	22
Iron	17
Mercury	2·6

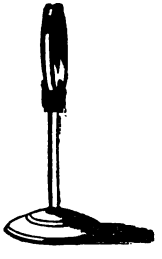
The Leyden Jar.—This powerful agent of electrical condensation involves no principle that has not already been described. Its construction is based upon a direct application of the laws of induced electricity. The casual examination, however, of a Leyden jar is suggestive of another idea—the idea of electricity as a material fluid capable of being preserved in vessels of capacity. It was this idea, indeed, which led to the discovery of the Leyden jar; the history of which is curious.

In the year 1743, Cuneus and Muschenbroek, of Leyden,* imbued with the sentiment then universally prevalent that electricity was a material fluid entity, bethought themselves of trying whether the fluid could not be accumulated and preserved in a non-conducting vessel filled with a conducting material. The vessel they employed was a glass phial—the conducting material water. Into the bottle a nail was thrust in such a manner as to establish electric communication between the conducting material (water) internally, and the charged prime conductor of an electrical machine. An experimenter now taking the bottle in his hand, and causing the nail to approach the prime conductor, drew electricity from that source until no more would flow—the bottle, to adopt the expression of a former period, being full. He now approached the knuckle of his finger to the nail, expecting, no doubt, to receive a spark of just the same force as he might have received from the prime conductor itself. Instead of this, however, he received a shock; and a new field of observation was opened. As the fullest details connected with the formation of this primitive electric bottle are on record, we may form a just appreciation of the power of the received shock. It must have been altogether insignificant; yet so great was its novelty, so unexpected its occurrence, that it terrified Muschenbroek extremely, so that he protested he would not receive a similar shock for all the kingdoms of Europe.

It must be confessed that a casual examination of the electric or Leyden jar is singularly suggestive of the idea that electricity is collected in it bodily. The idea, however, is soon dispelled by further investigation. If it were really true that the

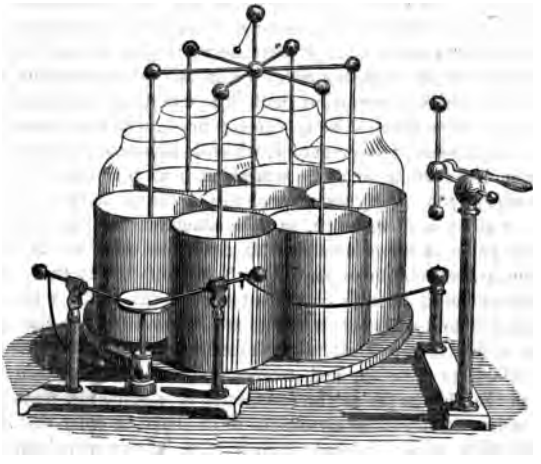
* "Hist. de l'Academie," 1746.

theory of this instrument be referable to the mere retention of electricity by a surrounding non-conductor, then it follows that the bottle should not require an outside coating: it would follow, moreover, that the thicker the bottle the better the effect. Neither is true. There must be an external conducting layer of some kind, and the glass must not be too thick. But in what did the external coating of the first Leyden jar consist? The hand of the operator himself; without which, or some equivalent, as was soon discovered, the experiment could not succeed. As at present constructed, the Leyden jar consists of a glass vessel or bottle, of about the usual thickness, coated internally as well as externally with tinfoil, which, however, stops short at a certain distance from the mouth of the jar: this distance, practice alone can determine. In making these jars, many practical considerations have to be regarded, which it is unnecessary here to state: it is proper to mention, however, as involving something more than making the jar, that it is a good plan partially to overlay the extreme edge of the tinfoil internally, with a slip of paper about half an inch in width, in such a manner that one-half of the paper, or a little more, may be in direct contact with the glass sides, whilst the remaining portion of paper surface is in direct contact with the tinfoil. By this contrivance, any little asperities or points existing on the cut edge of the tinfoil may be guarded, and thus their tendency to dissipate their charge greatly obviated. A similar adaptation might be made with increase of safety to the external coating also; but thus situated it would be liable to abrasion, and, moreover, the internal protection usually suffices. Regarding the Leyden jar as the application of a principle, we may now with advantage proceed to assume various alterations in its shape, in order that its dependence on electrical conditions already made known, may be the more lucidly demonstrated. Abandoning the obsolete theory which referred the concentration of electricity to the shutting up of the influence in a vessel of capacity, it would follow that, instead of a bottle, any double-coated layer of non-conducting material would be equally efficacious. Such, indeed, is the case; the form of glass sheet on which the conducting layer is imposed being purely a matter of convenience, a flat, doubly-coated sheet of glass, as represented in the subjoined diagram, answers perfectly well, and the slightest attention will at once show that such an arrangement is virtually that of Volta's condenser—a full description of which has been given at page 218, and which, by comparison with the Leyden jar, will be seen to bear out the remark. In the Leyden jar, or its analogue, the interposed non-conducting agent is glass; in Volta's condenser, the interposed non-conducting agent is atmospheric air. This difference, it will be seen, is not one of principle, but of construction: virtually, therefore, the two instruments are identical. After what has been stated concerning Volta's condenser, little remains to be said about the Leyden jar, the nature of which will immediately be evident. On bringing the knob *a*, which may be considered as an extension of the internal coating, in contact with the prime conductor, the internal coating receives a + or positive change, equivalent in power to the amount of — or negative influence susceptible of concentration in its vicinity. Now this amount of condensation will depend, *ceteris paribus*, on the extent and the proximity, within certain limits, of conducting surfaces;

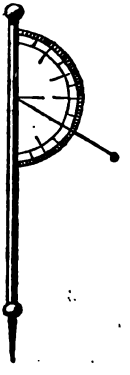


LEYDEN JAR.

and, inasmuch as the external or opposed metallic coating furnishes the proximity of surface under the most favourable theoretical conditions, the Leyden jar becomes adapted, according to a primary law of electricity, to receive the maximum amount of electric influence. If the glass, or other interposed medium, be too thick, then the power of the instrument diminishes, in consequence of the opposed metallic plate being too far removed. If, on the contrary, the glass be too thin, it is liable to be broken by the electric polar conflict which takes place amidst its particles. By increasing the dimensions of a Leyden jar, or (what amounts to the same thing) by increasing the number of jars in communication, the power of the combination may be increased to an extent only limited by the power of the machine employed in charging it. Such a combination of jars is termed the Leyden, or the electric, battery—an apparatus by means of which the most magnificent displays of electrical power may be evidenced, and all the tremendous effects of lightning imitated.

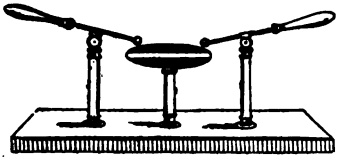


Method and Effects of Discharging the Leyden Jar or Battery.—The ordinary mode of ascertaining the degree of tension at which the electricity of a Leyden combination has arrived is by means of the Henley's quadrant electrometer, as it is called, an instrument which is represented in the accompanying woodcut, and the indications of which depend on the repulsion of a pith-ball attached to one end of a thin wooden filament, the other end of which turns on a vertical pivot. The deflections of this wooden filament are proportionate to the tension of electricity within the system; and being read off on a graduated ivory scale, the progress of the electrical charge may be approximately estimated. When the jar or system has been charged, it may be discharged by establishing a metallic or other suitable conducting channel between the two coatings. This, in the language of electricity, is denominated *completing the circuit;* and bodies on which it is desired to operate by means of the accumulated electricity must be made part of this circuit. Various methods are had recourse to for establishing this communication; but the instrument commonly employed is termed the discharger, represented on the following page. Mere inspection of this instrument will show that it is well adapted for the purpose intended. The distance between the outside coating and the knob communicating with the internal coating being judged of by the eye,

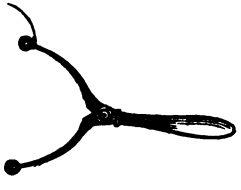


the brass arms of the instrument admit of regulation by means of the pivot from which they diverge; and the glass insulating handle obviates the chance of an electric shock, or the dissipation of passing electricity. When the instrument is thus applied to a charged Leyden jar or system, a report is heard proportionate to the tension of the electricity collected, a spark is seen passing through the air at the point *s*, electric equilibrium is restored, and the jar or system is said to be discharged.

Although the common discharger is sufficient for effecting the mere discharge of a Leyden combination, other instruments are necessary for the purpose of bringing the passing electricity into operation. Of these instruments, the one most generally required is known as Henley's universal discharger, and is represented by the annexed woodcut. The advantage of this instrument will appear in the course of experiments about to be described.



Some effects of Accumulated Electricity.—Provided the body through which electricity is transmitted be a conductor sufficiently good, and sufficiently large, the passage of accumulated electricity exercises no perceptible effect. This statement may be inferred from a consideration of the act of discharging a Leyden jar by means of the instrument just described, in which the electric force traversed the entire length of the brass arms, without permanently affecting them in the slightest degree. If those arms, however, had been sufficiently slender, there would have followed a different result. The metal would have been fused. This may be shown in the following experiments:—Employing a Leyden battery of not less than four jars, each having a capacity of not less than three quarts, prepare a metallic communication of the following kind:—To one arm of the discharger attach the end of some fine steel wire, such as is used for the balance springs of watches, bringing the other end of the wire into communication with the external coating of the battery. This can readily be accomplished by twisting the wire round the metallic hook, or stem, always attached to the case in which the jars of a battery are contained, and which is in immediate communication with their external coatings. Conditions being thus arranged, charge the battery, and discharge it in the ordinary manner. The conditions of the experiment are such that all the accumulated electricity must necessarily pass through the small steel wire, whose sectional area being very circumscribed, the electricity meets with interruption in its course, and combustion of the wire results.

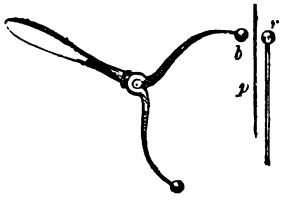


Instead of the wire employed in the last experiment, a slip of metallic foil, not too thick or too wide, may be attached by means of paste to a plate of glass or sheet of writing paper, and the electric influence transmitted, when the metal will be inflamed, provided the electric charge have been sufficiently strong.

In conducting this experiment, the mechanical disposition of parts will be facili-

tated by using the universal discharger already described. Not merely in these experiments does combustion result, but the electricity, whilst making its circuit, effects an expansion of the metallic substance, as may be rendered evident by the following experiment:—Attach as before a thin and narrow strip of metallic foil to a plate of glass, lay over it another plate of glass, and screw both tightly together by means of a little wooden press intended for that purpose. If the two glass plates be now laid on the table of the universal discharger, and the shock of a sufficiently powerful battery transmitted, not only will the foil undergo combustion as before, but one or both the glass plates will be fractured.

The fact has already been adverted to, that if the sides of a Leyden jar be too thin, they are liable to be broken by the force of electrical tension. The usual effect, indeed, of electricity, when made to pass through imperfect conductors, is to shatter or perforate. This may be readily demonstrated by employing a sheet of paper, or a card, to break the metallic continuity of an electric circuit, as may be readily effected by adopting the contrivance represented underneath, where the sheet of paper, *p*, is seen to be interposed between the ball of the discharger *b*, and the ball *r*, communicating with the interior lining of the battery. Leaving these exemplifications of consequences resulting from the electric discharge through bodies not endowed with any marked qualities of combustibility, we may now investigate the effects produced by similar discharges on bodies eminently combustible; and here we shall find that the result is greatly modified by the cohesive state of the bodies acted upon;—for instance, it will be seen that gases are more readily inflamed than liquids, liquids more readily than solids. To accomplish the inflammation of a gas by electricity a battery is unnecessary—a single jar is not even required, although in practical laboratory operations a small jar is generally used. The mere passage of a simple spark from the prime conductor to a metallic jet, from which coal gas issues, is generally sufficient to produce ignition. The finger knuckle may be made to yield the spark, provided the operator be insulated on a glass-legged stool. The mode of operating demonstrates no electrical principle which has not already been discussed; but it affords a very striking method of performing the experiment.



An inflammable liquid—such as ether—may also be generally ignited by means of a spark drawn from its surface, by means of the knuckle or a metallic knob. This experiment may be most readily conducted by placing a small metallic pan on the prime conductor of the machine, filling the pan with ether, charging the conductor, and drawing from the surface of ether a spark. The ignition of inflammable gases in closed vessels is an operation of frequent occurrence in chemical practice, and is most readily accomplished by means of the electric spark. The engravings on the following page illustrate the general disposition of apparatus for accomplishing the result.

The vessels in which the gases to be exploded are confined, consist either of glass tubes or stout glass jars, and are called eudiometers. Fig. 1 represents the kind of eudiometer most commonly employed in laboratory practice; it consists of a stout glass tube, having an internal diameter of about half an inch, and a length of six inches. Towards the closed end of this tube two platinum wires are inserted at right angles to the axis of the tube, and securely fixed in their place by fusing the surrounding glass. The open end of the tube is caused to dip in a vessel of mercury; by

which contrivance the interior of the tube becomes a cavity closed on all aspects. The two platinum wires which perforate the tube do not touch, but a small space remaining between them; a charge of electricity can only pass from one to the other in the form of a spark, by the agency of which combustion is effected.

Fig. 1.

Fig. 2 represents a form of eudiometer for which we are indebted to the ingenuity of Dr. Ure. The former instrument either requires to be firmly attached, by means of screws, to the mercurial trough whilst the electric charge is being transmitted, or the aid of an assistant is required. The employment of Dr. Ure's instrument renders these provisions unnecessary. The operator grasps the eudiometer firmly in his hand, closes the open end with his thumb, and draws the spark with his finger knuckle. The bend of the instrument contains a little mercury, which not only prevents the escape of gas, but deadens the shock occasioned by the exploded gas. Between the thumb and the corresponding surface of mercury there exists a column of atmospheric air, which acts the part of a spring, and serves to deaden the shock.

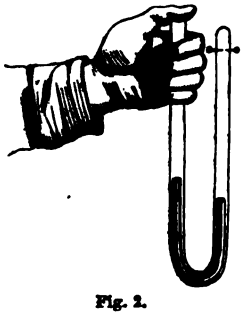


Fig. 2.

Fig. 3 represents a form of eudiometer devised by the celebrated Cavendish. It enables the explosion of considerable volumes of gas to be effected, and is, therefore, well adapted to the purposes of lecture demonstration. It was by means of this instrument that Cavendish demonstrated synthetically the composition of water.

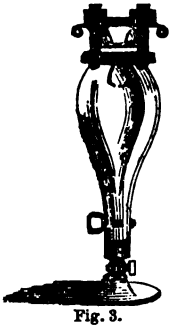
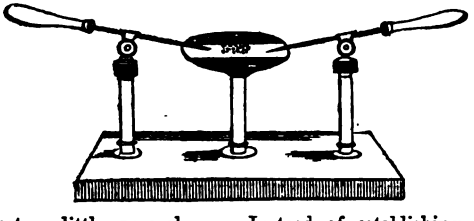


Fig. 3.

From examining the effects of strong electric discharges on gases and liquids, we next arrive at the consideration of its effects on solids; and of these we shall select gunpowder as the type of all the rest. For the purposes of this experiment, place a little gunpowder on the ivory portion of the table of the universal discharger, remove the brass knobs from the stem of the instrument, and establish a broken circuit, as represented in the diagram below.

By the term broken circuit is meant, that metallic communication stops short at either extremity of the little heap of gunpowder, which is itself an imperfect electrical conductor. Let a strong discharge be now transmitted, when the gunpowder will be scattered in various directions, but most probably it will not be inflamed. By slightly modifying the conditions of the experiment, however, it may be inflamed readily; and the modification taken in connexion with the result seems not a little anomalous. Instead of establishing direct metallic communication between the inside of the battery and the gunpowder, let a portion of the circuit consist of a piece of wet hempen cord. Most probably under this arrangement the



gunpowder will take fire. It will certainly do so if the length of string be duly apportioned to the strength of the discharge; this is a detail, however, which experience alone can regulate.

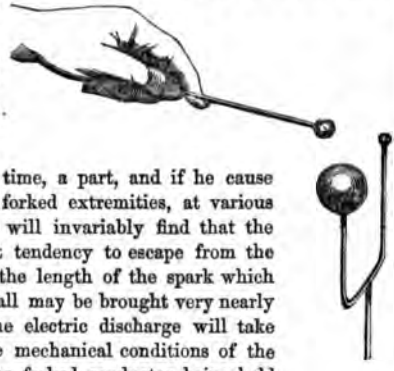
The result of this experiment, so seemingly anomalous, admits of very satisfactory explanation. The inflammation of gunpowder requires a certain prolonged application of heat; and this time is not afforded by the rapid passage of electricity as supplied under the conditions of the first experiment. When, however, the moistened string, which is a bad conducting channel, forms part of the circuit, then the electricity is made to linger in its passage, and ignition of the gunpowder results. There can be very little doubt that this is the true explanation of the phenomenon, inasmuch as the result is accordant with many analogies. Thus it is not easy to ignite gunpowder by rapidly passing over its surface a jet of burning coal gas, a certain appreciable lingering of the flame being necessary to insure the positive result. A more striking illustration is, however, afforded by the following experiment:—On a sheet of writing-paper lay a few grains of fulminating mercury in the form of a train; cross this train with another of gunpowder, and ignite the first. The flame passes with inconceivable rapidity from one end of the mercurial train to the other, the gunpowder being necessarily crossed by the line of fire; nevertheless the gunpowder itself does not inflame. Another illustration of the same fact is this:—If a percussion-cap, the charge of which is fulminating mercury, be placed on the nipple of a very short-barrelled pistol, a charge of powder thrown into the barrel, but no wadding, and the cap exploded, the gunpowder usually does not inflame. If wadding be rammed down on the powder, or if the barrel be prolonged, then the gunpowder is inflamed, because the blast of the percussion-cap is made to linger amongst the particles of gunpowder—in the one case, by reason of the superimposed wadding; in the other, by reason of the pressure of a column of atmospheric air.

Atmospheric Electricity—Theory of Lightning-rods.—It is almost unnecessary to state that the nature of thunder and lightning was totally unknown until the celebrated Benjamin Franklin identified them with electricity, thunder being the explosion, the lightning the spark. Hence these grand natural electric manifestations are identical, in all but difference of degree, with the report and the spark attendant on the discharge of a Leyden battery. It is also unnecessary to state that Franklin made this grand discovery by means of a kite, along the string of which the electric influence passed, and from the end of which he succeeded in drawing a spark.

The moment this discovery became known, an obvious means suggested itself of protecting buildings from the effects of lightning, by elevating, in contact with them, a metallic rod of sufficient dimensions to carry off the greatest charge of electricity that can occur at one time in a determinate area.

Great discussion originally took place amongst electricians as to the proper shape to be given to the extremity of these lightning conductors. One party advocated spherical terminations, *i. e.* knobs or balls; another, pointed extremities. There remains no doubt on this matter now. Points are universally accepted as being the preferable form, and the reason why they are preferable will readily appear from explanations which have been given before: an observance of the relative effects of points and knobs applied near to the charged prime conductor of the electrical machine at once settles the controversy. A more satisfactory way of demonstrating the relative influence of points and knobs, however, is supplied by the following experiment:—To the prime conductor of an

electrical machine attach the instrument represented in the following diagram, consisting of a forked conductor, each prong of which ends in a ball; but the balls are of different dimensions. Now it is evident that in proportion as a ball is diminished in size, so does it approach the nature of a point; founded on an appreciation of which circumstance is the experiment about to be described. If the operator charge the prime conductor, of which the forked apparatus is assumed to be, for the time, a part, and if he cause a knobbed conductor to approach the forked extremities, at various relative distances from each other, he will invariably find that the electric discharge manifests the greatest tendency to escape from the small ball; as may be judged of from the length of the spark which it gives off. In this way the moveable ball may be brought very nearly into contact with the large ball; still the electric discharge will take place from the small one. If desired, the mechanical conditions of the previous arrangement may be reversed, the forked conductor being held in the hand, the single ball conductor fixed; still the result will always agree in this—the electric discharge invariably manifests a relation of preference for the small ball.



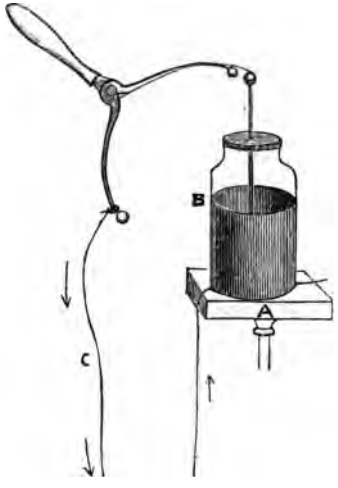
As regards the material of which lightning conductors should be constructed, this will necessarily be determined by a consideration of the relative conducting power of different bodies. Metals are pre-eminent as electric conductors; therefore a lightning-rod should be of metal, and amongst metals copper is the most eligible. In England, flat bars of copper are used; but, according to Mr. Faraday, a philosopher whose profound electrical investigations entitle his opinions to the greatest confidence, their usual dimensions are not sufficient, accidents having frequently occurred to buildings protected with rods of this kind.

A point of fundamental importance in the erection of lightning-rods is this:—They should at their inferior extremity be brought into direct metallic communication with the earth, by which is meant not merely the superficial soil, which may be of such a kind as to become, when parched and dried by continued heat, a conductor of electricity so imperfect that they may be altogether unable to carry away the electricity accumulated in the copper bar. By the term earth, is meant the whole mass of the globe in an electrical sense. If a mass of water be near, it is a good plan to extend the lower extremity of the lightning-rod into it. If the building to be protected be in a town, no better termination to the lower extremity of a lightning-rod can be given than the general system of gas or water-pipes, with which it should be brought into direct communication.

Another precept to be remembered in the erection of a lightning-rod is this:—It should be brought into metallic communication with every considerable piece of metal work in the edifice which it is designed to protect, otherwise the rod is a source of danger instead of an Ægis of safety.

The necessity for establishing this metallic communication, arises from what electricians call the lateral discharge, and which may be thus illustrated:—Let A represent a Leyden jar, B a copper wire on which it stands, and which is therefore in communication with its external coating. The copper wire may be indefinitely extended,

which extension the diagram is inadequate to illustrate. If the jar be now charged and discharged, the tendency of its electricity is to permeate the best electric conductor, which in this case is the wire; but even the best conducting body affords some resistance to the passage of electricity, so that it is possible for two parts of the wire circuit to be brought in sufficient proximity to each other so that the electricity rather passes in the form of sparks through the intervening layer of the non-conductor than along the lengthened circuit of the conducting material. The conditions of arrangement in the preceding diagram are such that the electric spark would pass at the point marked C. It is easy to apply the demonstration here involved to the actual case of a building to which a lightning-conductor has been applied.



Let A be a lightning-conductor penetrating the ground superficially; B a metallic water-pipe, having good metallic communication with the earth; and let a powerful shock of electricity strike on A from a thunder-cloud above. Under these conditions probably the electricity would force its way along and between the masonry of the house, between A and B, as represented by *n*, thus shattering the wall. In this case the lightning-rod has been the cause of the destruction of the wall. Had the rod not existed, probably the charge of the thunder-cloud might have avoided the building altogether, or, if it had struck the building, its discharge would have been determined by, and would have passed along, the most prominent metallic mass on the external part of the building, and which, under the conditions assumed, would have been the water-pipe.

It was customary formerly to insulate lightning-conductors, studiously avoiding all electric contact with the building, from which they were carefully separated by the interposition of non-conductors. This plan is not merely useless—it is injurious, *dangerous;* being directly opposed to the conditions necessary to be adopted for avoiding lateral discharge.

An important question for determination, relative to the practical application of lightning-conductors, is the following: What is the area of protection which a conductor of given dimensions is able to confer?

Towards the latter part of the past century, this question was investigated by the

French philosophers. They considered themselves justified in arriving at the conclusion that a lightning-rod might be considered protective to an area equal to twice the length of the lightning-rod, considered as radius. The deduction, however, is unsound, inasmuch as the result varies according to conditions; the protection being more or less complete according to the elevation of the rod, its size, its conducting power, the absence of other towering objects in its vicinity, and some other circumstances.

To demonstrate how small an area may be protected by a lightning-rod, by reference to what has occurred, the following example may be cited:—The mainmast of H.M.S. "Endymion" was protected, the foremast not, and a flash of lightning striking the latter, shivered it to atoms; yet the distance between the two masts was scarcely fifty feet.*

Hence large buildings will require a number of protectors proportionate to their extent, and an isolated column will be amply protected by one. It follows, moreover, that a column need not have an unsightly point elevated above its capital, or extreme termination; if the point be equal in height to that of the extreme capital, electrical conditions of safety will be fully satisfied.

Applying these remarks to the column represented by the accompanying diagram, the electrical conditions of safety may be readily traced out. Let A represent a lump of metal, C an intervening piece of masonry, and B a metal railing in direct electric communication with the ground by a specific rod, or some casual means, such as the iron stair-rail within. Provided free dispersive power were given to the lower end of the iron stair-rail, or other conductor, every portion of the column would be lightning-proof except the intervening masonry C, which being an imperfect conductor, would remain in extreme danger. Assuming A to be struck by an electric flash, the charge would rush across the masonry C, shattering it more or less; but the charge once arrived at B, would rush silently, harmlessly away. In order to insure safety, therefore, to every part of such column, it would have sufficed to interpose metallic connection between A and B. Not the slightest advantage would accrue from elevating an unsightly spike above A.

These conditions have been remarkably violated in the Duke of York's Column, St. James's Park, where a spike is made to project aloft from the head of his Royal Highness. The statue looks as if it were transfixed; thus violating the dictates of science, abusing art, and suggesting ideas of an impaled malefactor.

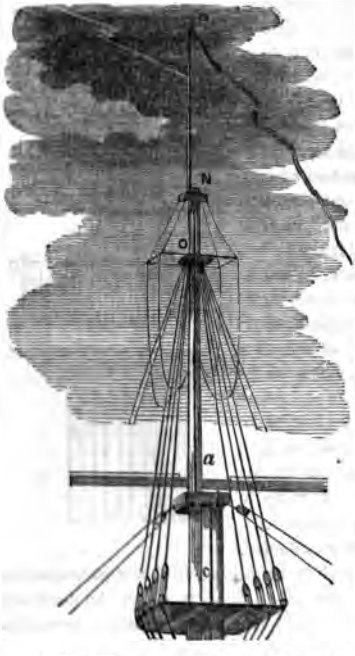
Marine Lightning Conductors.—It will be readily seen that a permanently elongated rod of metal is inapplicable to the protection of ships, in which the necessity for elevating and lowering the masts would be incompatible with this arrangement. A metallic chain affords a more practicable substitute; although, regarded merely in relation to power of conducting electricity, a catenary relation of parts is much less efficient than a continuous unbroken arrangement, such as is afforded by a metallic rod; moreover, chains, although not altogether incompatible with the mechanical

* Harris, "On the Nature of Thunderstorms."

arrangements to which ships are limited, are exceedingly inconvenient. Nevertheless, anterior to the adoption of the permanent marine lightning-conductor of Sir W. Snow Harris, chains were used, not permanently attached to the masts, or holding any permanent relation to the rigging, but elevated at the season of supposed danger. The objections to conductors of this kind will readily be anticipated. Not only were they inapplicable to many cases of sudden thunder-storms, but their erection was always a work of extreme danger, as the numerous accidents, of which they have been the direct cause, will abundantly testify. Added to this, the fundamental objection to the catenary arrangement, and it may be doubted whether, viewed impartially under all aspects, chain lightning-conductors have not occasioned more accidents than they ever prevented.

Sir William Snow Harris has imparted to marine conductors all the advantages of those on land by the simple expedient of inlaying a slip of copper along the whole length of each mast; and the copper slips of each mast are so arranged, that, under all amounts of elevation or depression to which the masts are subject, the metallic contact between the adjacent copper slips is invariably preserved.

These permanent marine conductors were at first strongly objected to. They were assumed to attract electricity needlessly, when, perhaps, had they not been in existence, lightning would not have struck. Moreover, the plan adopted by Sir W. S. Harris in establishing connection between the lower part of his marine conductors and the sea involved a direct passage of the copper plate through the ship, and not over the sides, as heretofore. This plan was objected to as dangerous by persons who were not familiar with electrical laws. No danger, however, can arise, provided the conductor present a sufficient metallic thoroughfare to the electricity; otherwise it is true, under favourable conditions, a transverse discharge might occur.



As regards the supposed *attraction* of lightning, said to be caused by conductors, this is not strictly true; the lightning is not attracted, but simply offered a road, wherein it may escape.

The following relation of a lightning stroke which fell on H.M.S. "Conway," so strikingly illustrates this proposition, and bears such general evidence to the value of permanent marine lightning-conductors, that I quote it from the original treatise of Sir W. S. Harris:—*

"The ship was moored in the harbour of Port Louis, in the Isle of France. The topgallant masts being on deck, for the refit of the rigging, a small boom (not having any conductor on it) was set up at the main-topmast head as a temporary flag-staff, as

* "On Protection of Ships from Lightning." London. 1847.

shown in the preceding cut. Under these circumstances, the ship was struck by lightning at 11h. 45m. A.M. of the morning of the 9th of March, 1846. The results were, that the flag-staff without the conductor was shattered in a thousand pieces, but only so far as the point N at the head of the topmast. At this point the destructive action was arrested; but here also commenced the line of electrical conduction, N *a c*, by which the whole charge was carried clear off into the sea, covering the waves on its exit from the side of the ship with a blaze of brilliant light. Nothing could be more perfect than the protective action of the metallic conductors.

"It is important to remark, as a confirmation of the result given in the case of the 'Fisgard' (similar in all general particulars to the result now under consideration), and other cases, that the gunner, at the time of the discharge, was sitting in his cabin, immediately under the beam along which one of the main branches of the conductor passed. He describes the effect as being that of a pistol fired at him close to his head, which so startled him that he fell back on the arm-chest. The scuttle being open, he observed, at the same instant, a brilliant blaze of light burst from the ship's side upon the water; but experienced no sort of inconvenience whatever. It is important to notice this fact, as it completely disproves the assumption that efficient lightning-conductors frequently produce lateral discharges upon bodies in their vicinity, and that persons near such conductors are in danger of being destroyed."*

Velocity of Electricity.—Until the year 1833 the rate of velocity with which electricity traverses conducting bodies was unknown, although many philosophers had applied themselves to the task of investigating this point, and the electric current was timed in its passage through several miles of copper wire. The time of entrance and emission, however, as marked by the accompanying spark, always seemed equal. Eventually the idea of attempting to discover this rate of velocity became generally abandoned, for what hope was there of estimating the velocity of such an agent, seeing that the efforts of philosophers must, after all, be restricted to the limit of an extension of wire? It is otherwise in estimating the velocity of light; here we have the diameter of the earth's orbit as our measure, and we trace the subtle element through space from other worlds to our own. But all investigations as to the velocity of electricity are necessarily circumscribed by the narrow limits of our own planet; hence the solution of the problem seemed hopeless. Professor Wheatstone, however, having applied his mind to the subject, the velocity of electricity was determined in a manner no less simple than beautiful. He reasoned thus:—If electricity takes time to travel, a charge transmitted through a circuit broken in two points cannot appear at both points at once. Such a conclusion necessarily follows from the premises; there is no alternative. If no distinction of time has been recognised, this circumstance may be attributable to imperfection of the means at our disposal for testing the fact. Professor Wheatstone, therefore, applied himself to the discovery of more delicate means of investigation than philosophers had hitherto employed, and ultimately he adopted the following happy expedient:—Several miles of insulated copper wire being wound round a disc of wood, the coils were so arranged that certain interrupted portions of them corresponded with one straight line. Now each interrupted portion would neces-

* The reader who is desirous of further studying the theory and practice of marine lightning-conductors may consult the following authorities:—"Observations on the Effects of Lightning on Floating Bodies." 4to. London. 1823. Harris. "Remarkable Instances of the Protection of certain Ships of Her Majesty's Navy from the destructive effects of Lightning." 8vo. London. 1847. Harris.

sarily correspond with an electric spark, on passing the discharge along the wire; and supposing electricity to occupy time in travelling, these sparks must occur successively. Hence the proposition resolved itself into a discovery of some means of estimating the succession. Mere chronometric observation would have been totally inadequate to this end, as previous experiments had demonstrated—some other plan was required.

Now, instead of viewing the sparks directly, they may also be viewed as reflected by a mirror. If reflected by a mirror at rest, no point would have been gained; but provided electricity occupied time in travelling, some evidence of this might be anticipated *à priori*, by viewing the sparks as reflected by a mirror in rapid rotation, for whilst the electricity had been occupied in travelling between successive portions of the wire, the mirror would have been performing its revolutions; and having reflected one spark at a determinate angle on a certain part of the screen, it would have reflected the second spark at another angle on another part of the screen, not in the same line with the first point. Therefore, supposing the result to be as here assumed, and which is actually the case, the elements for calculating the velocity of electricity under the conditions of the experiment are supplied; the data of subsequent calculation being the length of wire between spark and spark, and the velocity of the revolving mirror. Professor Wheatstone found that the reflected sparks were no longer in the same line, but supposing them originally to have constituted a vertical arrangement ⁝, their reflected images assumed the form of a letter V (:·).

This beautiful result demonstrated two points. Firstly, it demonstrated that electricity does not pass instantaneously through copper-wire; secondly, it demonstrated that electricity—whatever may be its real nature—proceeds from the two extremities of a conductor towards the centre of its length: otherwise the reflections would not have assumed the form of a V, but would have appeared in a diagonal line ⁘.

The data of this experiment enable us to arrive at the conclusion that electricity either travels through copper-wire, of the diameter used, at the rate of about 300,000 miles per second; or double that rate, according as we adopt the theory of one or two electric fluids. At the lowest estimate, then, it cannot travel at a slower rate than 300,000 miles per second, whilst light travels at the rate of less than 200,000 miles in the same time.

Electrical Theories.—In discussing the phenomena of a power so subtle as that of electricity, it is impossible to avoid falling into the language of theory, even though the theory itself be not accepted as true. Throughout the foregoing pages it has been endeavoured to avoid the adoption of theory as much as possible. Accordingly, the duality of electric force, which is its most fundamental quality, has generally been indicated by two letters, A and B. Occasionally the terms vitreous and resinous have been employed, also the terms positive and negative; but always under the assurance of their conventional use merely, and without assuming their employment to involve any theory. It will be necessary, however, in the chapter on galvanism or voltaic electricity to use the language of theory more generally than heretofore; without its adoption as a gross method of communicating ideas it would be exceedingly difficult, if not impossible, to expound important phenomena.

Any one who has studied the phenomena of electricity with moderate attention, cannot have failed to associate with this agent the idea of a fluid physical entity—of something that admits of being collected together like water in a pond, and of flowing on, when set free, like water in a river. Hence, the term electric fluid was, very early in

the history of the science, adopted, and was long accepted as the representative of a real physical entity.

But the assumption of one fluid, except under certain stipulations, is incompatible with actual phenomena. We have seen electricity to be a dual force; that one kind of electric influence cannot exist without a proportionate amount of the other being also brought into operation. This duality is a fundamental quality of electricity, also of magnetism, and is the grand distinction between them and the force of gravitation. Two theories of the electric fluid have been adopted,—one by Franklin, the other by Du Fay. The latter philosopher accounted for the dual manifestations of electricity, by referring them to the operation of two actually distinct electric fluids—the vitreous and the resinous.

Franklin, on the other hand, accounted for the phenomena on the assumption of one fluid alone; and as this fluid was present in excess or the reverse, so he imagined would be the electric result. So long as a body held its normal amount of electricity it might be compared to a hollow air-vessel in which the aërial charge was neither increased by compression, nor diminished by exhaustion;—whereas the A point of electric duality, according to Franklin, may be assimilated to the same air-vessel into which an additional charge of air had been condensed; and the B point of electric duality to the vessel when partially deprived of its air by exhaustion. Accordingly, the theory of Franklin naturally introduced the terms *positive* and *negative* as synonymes of the *vitreous* and *resinous* electricities of Du Fay.

It would be futile at this time to discuss the relative merits of these theories. Suffice it to say that the one fluid theory is incompetent to explain various electrical phenomena; it is incompatible, for instance, with the result of testing the interior of an electrified cylinder by means of a carrier-ball.

The two-fluid theory more nearly accords with the facts of electricity as evidenced; but the opinion seems gaining ground that electricity is not so much an entity within matter, as a condition of matter, and that its effects are most probably referable to an assumption and subsequent resolution of polarities.*

The adoption of this view very materially explains the existence of a seeming current, as a simple experiment will testify. Let a series of cards be arranged, as indicated in the accompanying diagram, under which arrangement they may be said to be *polarized* in relation to themselves. If the first pair in the series be thrown down, all the others must necessarily follow; and, this occurring successively, would give rise to the idea of a current.

Without adopting any theory of the electric fluid—without even taking for granted the existence of such fluid or fluids—it will be generally convenient to adopt in the section on galvanism the language of Franklin—to consider electricity as one fluid entity, and thus to trace the flow of an imaginary current in one direction only. It would be improper to close this branch of our subject without stating that the repudiation of the existence of a special electric fluid or fluids is warmly advocated by several philosophers, especially by Mr. Grove, a philosopher whose investigations on the subject

* For some highly philosophic speculations on electricity considered as a force, the reader may consult "Grove on the Correlation of Physical Forces."

of electricity and its alliances are so well known. It would be incompatible with the limits of this treatise to reproduce this gentleman's arguments; but they will be found in his "Correlation of Physical Forces."

Galvanic or Voltaic Electricity.—Although the sources of electricity in nature are numerous, the physical experimenter commonly avails himself of two—*friction*, and *voltaic* or *galvanic combination*. The origin and history of the latter are as follows:—In the year 1790, Galvani, a professor of anatomy at Bologna, whilst engaged in the dissection of a frog, observed the animal's legs to be spasmodically affected when their crural nerves were touched in a peculiar manner. Subsequently he found that the result could be rendered still more manifest by employing two metals instead of one (the knife-blade) for establishing contact. He found that zinc and silver were especially adapted for producing these contractions, one metal being brought into contact with the crural nerve of the frog's thigh, the other with its muscular tissue. Speculating on this curious phenomenon, Galvani referred it to electricity—a supposition long since proved to be correct. He imagined the source of this electricity to be the animal itself, and that the metals were only efficacious in affording a conducting channel to this electricity. A further exposition of the theory of Galvani belongs rather to physiology than to physico-chemistry; but an outline of it is as follows:—He assumed the brain to be a source of electric influence, which was distributed to all parts of the body, more especially to the muscles, the ultimate febrils of which he assumed to be hollow, and, like the electric jar, capable of receiving a charge by reason of its two opposed surfaces. The nerves Galvani believed to have the function of electrical dischargers—that they effected an electric communication during life between the internal and the external surface of muscular febrils, and thus produced the electric discharge. Finally, he believed that a metal might be caused to assume the function of a nerve—namely, to effect communication between the electrically opposed surfaces of the muscular febrils.

Any theory which does not embrace all the known phenomena of the subject to which it refers must be evidently unsound, and the theory of Galvani is open to this remark. Judged even by the evidence known to Galvani, the theory was incomplete. It failed to attach importance to the increased muscular effect resulting from the contact of two metals. Moreover, it was based on a *petitio principii*. The brain had neither been proved to be a source of electricity, neither had it been demonstrated that the muscular febrils were hollow—nor that one portion of a muscle was a non-conductor, other portions being conductors; finally, it had not been demonstrated that nervous matter was pre-eminently endowed with the quality of electric conduction. The extraordinary nature of Galvani's experiments brought several investigators into the field, and amongst them several opponents. Some of these denied that the results were in any way referable to electricity; others, admitting their electrical origin, referred the electricity to other sources than that indicated by Volta. Amongst the former was Fabroni, who attributed the animal contractions to the effects of heat developed by oxidation of the metals employed. Amongst the latter was the celebrated Volta, who attributed the electricity to metallic contact; and if he did not strengthen his own theory, he at least annihilated those of Galvani and of Fabroni, by demonstrating that the electrical influence might be increased proportionately with an increased number of metallic reduplications. He took discs of silver and zinc, or copper and zinc, arranged them vertically in pairs, with moistened discs of flannel between each pair. The apparatus thus generated, manifested powerful electrical effects, and, in

honour of its discoverer, became known as the Voltaic pile. Although the structure of this instrument was diametrically at variance with the theories of Galvani and Fabroni, it was not less at variance with the theory of Volta himself. It has been stated that the instrument can only be brought into activity by the interposition of a moistened disc of flannel, or other absorbent material, between each pair of plates.

The theory of Volta evidently affords no *rationale* of this; and it is still more incompatible with the fact hereafter discovered, that the interposed moisture must be of a kind that exercises some chemical effect on one of the metals. Hence three questions present themselves for investigation; they are these:—(1). Is metallic contact a source of electrical power? (2). Is the electrical power from mechanical contact aided by chemical action? (3). Is the electrical disturbance referable to chemical action alone?

These three questions, variously agitated, have been prominent topics of investigation ever since the time of Volta, and have entered as elements into all subsequent theories of voltaic excitation. These theories will be further adverted to in their proper place; meantime, it may be desirable to state here that the theory which attributes all the resulting electrical excitement to chemical action is that most usually, if not universally accepted at the present time.

Simple and Compound Voltaic Combinations.—A simple voltaic combination is that in which the smallest number of parts compatible with manifesting the voltaic result is employed. For example, two metals, and a fluid chemically affecting one of them, is a simple voltaic arrangement, as, in like manner, is a metal placed in relation to two different chemical fluids, each exercising its own specific action. A compound voltaic arrangement is one consisting of many simple arrangements aggregated into one instrument. Thus a single piece of zinc brought into mediate or immediate contact with a piece of silver or copper, and both metals immersed in a liquid capable of acting chemically on the zinc, constitutes a

Fig. 1.

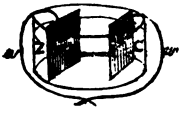


Fig. 2.

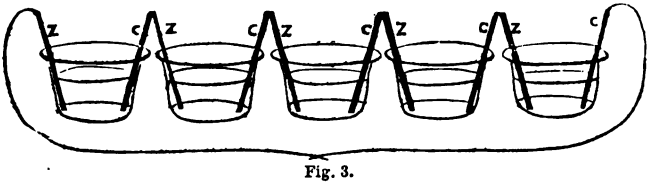


Fig. 3.

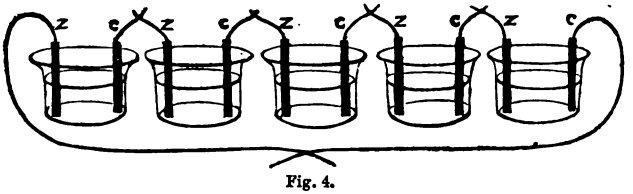


Fig. 4.

simple voltaic arrangement. The annexed diagrams further illustrate this point. Fig. 1 represents a simple voltaic arrangement by immediate contact; Fig. 2 a simple

voltaic arrangement by mediate contact; the intermediate substance being the wires *w w*.

Figures 3 and 4 represent compound arrangements resulting from an aggregation of the two varieties of simple ones previously depicted.

It has been already stated that the language of Franklin's one-fluid theory affords considerable facilities in the description of voltaic phenomena. I shall, therefore, unreservedly adopt it, with the express understanding that the adoption is made solely with a view to facility of description. Speaking, then, according to the language of this theory, every voltaic arrangement may be regarded as furnishing the conditions of a circuit along which the current of electricity passes, and this circuit may be closed or broken. Thus Fig. 1 represents a closed, Fig. 2 a broken circuit. Along this circuit, whilst closed, a continuous electric current passes, in tension proportionate to the number of combinations simultaneously acting, in quantity proportionate to the area of metallic surface, and the character and power of those chemical actions which are associated with the activity of the voltaic combination. It is desirable to acquire settled notions concerning the direction of this electric current; and a simple method exists of fixing this information in the mind:—*The current passes from the metal subject to greatest chemical action to the liquid, thence to the second metal, and so forward.* Now, in a voltaic combination of zinc, copper, and dilute sulphuric acid, the metal chiefly, indeed entirely, acted upon is zinc; therefore, according to the rule just laid down, the current should pass from the zinc to the dilute acid, thence to the copper. It does so—in short, the rule is never violated; hence, being remembered, it defines the direction of electricity in all voltaic arrangements, however complex their several parts may be. Much confusion of language has arisen, and considerable difficulties have been imparted, by departing from this simple rule of guidance, and applying the terms positive or negative as absolute instead of relative designations. From a consideration of what has been said, the starting point of electricity, in every voltaic arrangement consisting of copper, zinc, and dilute sulphuric acid, must be zinc, *where that metal is in contact with the fluid.* Hence this may be termed the *beginning* of a voltaic arrangement; but the zinc can only impart electricity by losing electricity—therefore zinc is the positive metal in such a battery, although constituting the negative end or pole of the battery. This will be evident on the slightest reconsideration of the parts of which a voltaic battery is composed.

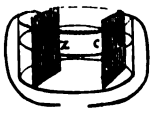


Fig. 1.

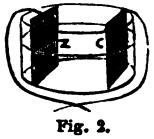
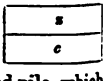


Fig. 2.

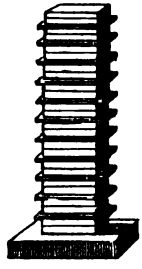
Another source of confusion has arisen in applying the terms positive and negative to the extremities or poles of voltaic arrangements, owing to the different theories prevalent in relation to the cause of voltaic energy. Thus, Volta himself, as I have before stated, attributed this energy to metallic contact alone. Hence, according to his views the simplest possible combination of zinc and copper would have been as follows:—



Reduplicating these simple arrangements, Volta arrived at his compound pile, which is represented on the following page.

In this arrangement the electric current traverses upwards; consequently the zinc end or pole of the pile is positive, and the copper end negative. But supposing Volta's theory to be incorrect—supposing the electric force not to originate from metallic contact, but from chemical action, then it follows that the extreme plates of the arrange-

ment may be removed without prejudice to the result, when the copper end would become positive and the zinc end negative. If the fact, however, be always remembered that the electric current passes in the manner already described, no ambiguity can arise.



The statement has been already made that the tension of electricity developed from a voltaic battery is, *ceteris paribus*, in proportion to the number of combinations; hence it follows that in proportion as the number of combinations is great, so do the results of voltaic electricity resemble more those produced by frictional electricity. This fact is strikingly borne out by every phase of voltaic manifestation. A battery consisting of only a few pairs of large plates, and which gives rise to the most stupendous physical effects—such as the fusion of platinum bars, of clay, &c.—is incapable of giving the electric shock, deflecting an electrometer, or imitating in any manner the results of frictional electricity. Provided, however, a sufficient number of combinations be aggregated, the ends of the poles of such a combination are able to affect the electrometer, and thus the kind of influence proper to each pole may be determined. Since the discovery of the galvanometer, however, an instrument which will be described further on, a far more practicable means exists of determining the quality of electricity proper to each end of a voltaic battery.

Effects of Voltaic Electricity.—These may be conveniently divided into physiological, electrical, chemical, and magnetic.

The *physiological* effects of voltaic electricity chiefly refer to the production of involuntary muscular contractions, and of shocks similar to those produced by a Leyden jar. The kind of battery best adapted for this class of experiment is one composed of a large number of series—not less than two hundred—but the individual size of each of the series need not be large, nor is it necessary to employ, for exciting the apparatus, a chemical mixture of great strength. The most convenient form of construction for a battery of this kind will be made apparent hereafter, when the different existing varieties of voltaic apparatus are explained; and the physiological agencies of voltaic influence being remote from chemistry, the few remarks already made under this head will suffice.

The electric effects of voltaic energy resemble those produced by the ordinary machine, more closely as the number of voltaic combinations is greater; the similarity of effects, in other words, is proportionate to the number, without reference to their size. When the combination is sufficiently numerous, all the effects of frictional electricity may be produced, and conversely, as Dr. Wollaston has shown, all the effects of voltaic energy may be produced by employing frictional electricity with certain necessary precautions. The determination of these points was very necessary, in order that the identity of voltaic influence and electricity might be established. At present the identity is demonstrated beyond all controversy.

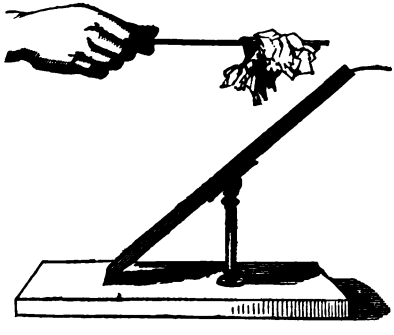
Although the electrical effects of voltaic arrangements may be accomplished by the ordinary machine, yet the variation as to degree between these classes of effects is so very great, that certain phenomena may be practically considered as belonging especially to the effects of voltaism.

Combustion and Incandescence.—In the section of frictional electricity, the power of that agent in effecting combustion of substances under given conditions was shown. The result was demonstated to be, *ceteris paribus*, proportional to the obstruction opposed

to the electrical current in its passage; hence, its combustive efforts were limited, so far as relates to conductors, to those having a small sectional area. The quantity of electricity capable of generation in a given time from our largest voltaic arrangement, is greater, beyond all calculable proportion, than that from our largest electric machines; hence, the combustive effects of the voltaic battery are very brilliant.

A few experiments may now be given indicative of the chief phenomena of voltaic combustion and incandescence. As a special description of the practical construction of voltaic batteries will be deferred to a further part of this section, it is desirable to state that the best kind of battery for developing the effects presently to be detailed, is the invention of Mr. Grove. Of all known arrangements, this battery evolves the greatest amount of voltaic influence in a given time, and from given dimensions. A minute description of Grove's battery will be given hereafter; meantime it is necessary to state that, amongst other variations from the materials of the voltaic arrangements already noticed, there is the important one of substituting platinum for copper.

For the first experiment, *the deflagration of metallic foils*, it is desirable to provide a polished metallic plate, about 3¼ inches wide by 12 or 15 long, and soldered at one extremity to the positive wire or pole of the voltaic battery; inclined, when used, by any convenient support at an angle of about 45°. The metallic foil to be deflagrated is now attached to the extremity of the negative wire, and brought into contact with the plate. Deflagration will immediately ensue, if the battery be in good working condition; but, in order to secure its equable continuance, the foil requires to be brought into contact with different portions of the metallic surface, inasmuch as the deflagration being attended with oxidation of the metal, dulls the plate, and thus prevents good metallic contact. In these and similar cases of voltaic combustion, the amount of effect is proportional to the amount of electricity which passes, and this is proportional, chemical action being equal, to the size of the plates, independent of their number; but, on the other hand, a certain amount of intensity requires to be given to the voltaic influence in order to enable it to force its way through any badly conducting body which may lie in its path. For example, referring to the last experiment, it would be found that if a voltaic combination of only one pair of plates had been used, the resulting influence would scarcely have been able to force its way through the superficial coat of dulness which collects, owing to oxidation and other causes, on the surface of all metals. By increasing the number of combinations to five or six, the degree of intensity is imparted necessary to overcome those casual obstacles. Still, even under the latter circumstances, so feeble is the tension of the passing electricity, so slight its endeavour to escape, that the conducting wires of the battery may be handled without communicating a shock to the operator, and without dissipating the voltaic current which is passing. Frequently the prosecution of experiments with voltaic electricity of weak tension is facilitated by amalgamating the metallic bearings, by which treatment absolute metallic contact is insured. For extemporaneous dispositions of apparatus, this treatment is sometimes

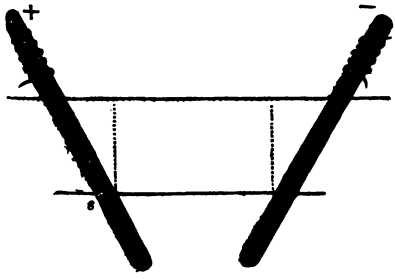


desirable; but, generally speaking, recourse should not be had to the expedient in instruments of costly nature and limited power of accommodation between their points of adjustment. Amalgamation, in the latter case, rapidly destroys the bearing surface, and thus the instrument, although more powerful at first than it would have been had mercury not been used, is rapidly destroyed. Whilst performing the deflagration of various metals, the experimenter will observe each metal to burn with evolution of its own peculiar light. Gold leaf evolves a bluish-white light, crumbling into a dark-brown oxide; silver yields a light of an emerald-green colour; copper burns with a bluish-white light, attended with the evolution of sparks; lead evolves a purple; and zinc a brilliant white light inclining to blue, and fringed with red.

The deflagration of steel wire, which required such considerable power of frictional electricity, may readily be accomplished by means of voltaic influence, even with a battery of small dimensions. The best way of conducting this experiment consists in establishing contact between the steel wire and a surface of mercury in communication with the negative end of a voltaic battery, as represented by the accompanying diagram.

Substituting other metallic wires, each metal will be seen to have its own measure of voltaic combustibility; and on referring to a list of conductors, arranged according to their conducting power, it will be found that the metal which conducts electricity least perfectly is the most easily deflagrated. This result is consonant with what we have already seen in our investigations of frictional electricity.

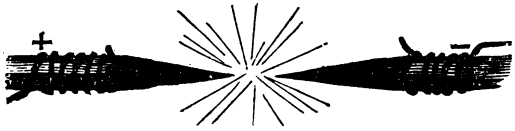
By arranging two metallic bars as represented in the diagram, the relative difference of combustibility subsisting between different metallic wires of equal size may be readily appreciated. Supposing platinum wire to be stretched across these slanting metallic bars in contact with both, at the point represented in the diagram, and to become barely incandescent, then silver wire, in order to be made incandescent to the same extent, must be held firm down in contact with the bars, at a point where the distance between them is less, as represented at *s*; and the difference between the length of silver wire and the length of platinum wire—thus rendered equally incandescent by the same battery-power—may be considered proportionate to the respective capacities of silver and platinum for conducting electricity.



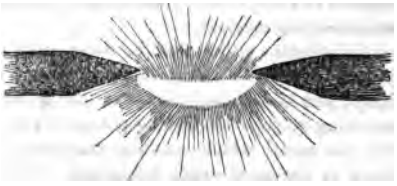
A very elegant way of demonstrating the fact deduced from the last experiment is as follows:—Procure some

pieces of platinum and silver wire of equal dimensions, and twist their ends together in such a manner that a compound arrangement may result; and suspend the combination by either end from the terminal wires of a voltaic battery in action. If the dimensions of the wire be correctly apportioned to the power of the battery, all the silver lengths will remain obscure, whilst all the platinum lengths are illuminated. The experiment, if performed in a darkened apartment, is very striking.

The most brilliant effect of voltaic combustion, or rather incandescence, results from causing the influence to pass between two charcoal points, attached respectively to either terminal wire of a voltaic battery.



When the apices of two conoidal pieces of charcoal are brought into contact, after having been attached to the terminal wires of a voltaic battery in operation, as represented in the accompanying diagram, a vivid spark appears, and the charcoal points immediately assume a most vivid state of ignition, without suffering combustion at all proportionate to the light evolved; indeed, if the charcoal points be immersed in oil, in water, in vacuo, or in hydrogen or nitrogen gases, the same brilliant light, slightly modified, is evolved—a fact which sufficiently proves the phenomenon not to be entirely referable to ordinary chemical combustion. If the battery employed for the performance of this experiment be of adequate strength, the charcoal points may be separated considerably from each other, when a broad and vivid arc of flame, possessing extraordinary heating power, joins the two charcoal points; and the most infusible bodies, when placed within the limits of this arc, are either fused or dissipated in vapour.



All charcoals do not answer equally well for this experiment; the facility of incandescence being almost directly proportionate to the density of the charcoal. Hence that resulting from the destructive distillation of box-wood or lignum vitæ is the best that can be made from wood. It is necessary, also, that the charcoal be thoroughly well burned—for which purpose the box-wood, or lignum vitæ, may be imbedded in a crucible full of sand, and exposed to an intense furnace-heat.

The best sort of carbonaceous matter for the purpose is made by burning a mixture of sugar and powdered coke.

The light developed from such incandescent charcoal points is so intense, and the primary colours are so well mingled, that it would seem admirably adapted for purposes of illumination. All attempts, however, hitherto made in this direction have practically failed, chiefly on account of the intermittent nature of the light—a consequence of the gradual destruction of the charcoal terminals, and the ever-varying contact resulting. Some ingenious mechanical contrivances have been adopted to remedy this latter defect; and a certain amount of regularity of incandescence has been gained by employing the dense artificial carbon of sugar and coke: the objection, however, has not been overcome. If the electric light should be rendered intermittent, the economy of its application would constitute the next point for determination. It would be necessary to

employ a battery of such kind that the product of solution going on within it should be commercially available; and the proceeds of its sale, together with a fair remuneration for the light evolved, should cover the total expense of apparatus, wear and tear, and superintendence.

The chemical agencies of voltaic electricity are very remarkable. Their discovery was first made in this country; the development of their laws is also chiefly due to our own philosophers; and perhaps the most brilliant discovery ever made in chemistry was the result of successfully applying them—I allude, of course, to Davy's master-discovery of potassium and sodium.

The first chemical agency of the voltaic battery which came under the notice of philosophers was the decomposition of water. This discovery was made, in the year 1800,* by Messrs Nicholson and Carlisle, who, operating with a common voltaic pile, composed of zinc and copper pairs, with moistened flannel between, perceived the odour of hydrogen gas. They naturally assumed that the hydrogen thus liberated must come from the water employed to moisten the plates, and that the decomposition of water must be referable to the agency of the pile. Prosecuting their inquiries, these philosophers next tried the effect of passing the voltaic current through water, causing it to form part of a circuit, whereupon they demonstrated the correctness of their previous supposition—water was decomposed; and by slightly varying the form of apparatus, hydrogen and oxygen gases were separately collected.

The accompanying woodcuts illustrate the means of performing both these experi-

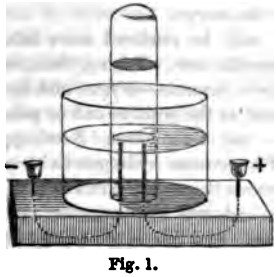


Fig. 1.

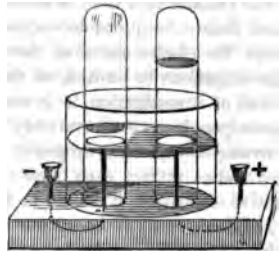


Fig. 2.

ments; Fig. 1 referring to an arrangement by means of which water is decomposed, and its constituent gases collectively obtained; Fig. 2 to a modification of that apparatus, by means of which the two gases may be obtained separately.

The preceding, and all other decomposing effects of voltaic electricity, take place in imperfectly-conducting bodies, in which the electric current meets with a certain amount of impediment during its flow. The obstruction, however, requires adjustment, in order that the operation may succeed. Certain bad conductors require to have their conducting powers increased in order that energetic decomposition may take place. Water is of this kind. Considered in relation to electricity of high tension, such as that produced by the ordinary electrical machine, water is a very good conductor; but considered in relation to voltaic electricity of low tension, it is not. If, therefore, the

* "Phil. Mag.," vii.; and "Nicholson's Journal," 4to, iv., 1831. Subsequently, the chemical effects of voltaic electricity were more accurately examined by Hisinger and Berzelius ("Gehlen's Journal," i. 115).

battery do not consist of a great number of plates, the decomposition of water will not readily be accomplished, without increasing the conducting power of that liquid. This is usually effected by the addition of a little acid, or common salt.

When the decomposition of water is effected in an apparatus which admits of the two gases being evolved and collected separately, it will be readily observed that the hydrogen is invariably liberated from one end of the battery, oxygen from the other. It will be seen, moreover, that hydrogen invariably corresponds with the negative, oxygen with the positive end: the question, then, naturally arises, why this apparent election? The question involves an important theory of chemical combination, proposed by Davy, and called the *electro-chemical theory*.

Accepting the voltaic decomposition of water as the starting point of further investigations, and extending the observation of parallel experiments to other cases, it will be found that the decomposition of compounds, when submitted to the agency of voltaic power, is general, not special. Not alone is it exercised on water, but the decomposition extends to numerous other compounds. The function, however, is not extended to all chemical compounds; and therefore, though general, is not universal, as Davy imagined it to be. Any theory, then, which associates with an entire range of phenomena of one class a function only having reference to a part of them, must necessarily be defective. The electro-chemical theory of Davy is in this position.

The chemical decompositions resulting from voltaic influence led this philosopher to imagine that electrical attraction and chemical affinity were identical; and he applied some of the fundamental laws of electricity to an explanation of the chemical union of bodies, and their subsequent decomposition by voltaic energy.

Perhaps the electro-chemical theory of Davy will be rendered more intelligible if our investigations be limited, at first, to one specific case. Taking, then, water as our material of investigation, it is composed of two elements—oxygen and hydrogen. When decomposed, oxygen invariably liberates itself at the positive end or pole of the voltaic arrangement, and hydrogen at the negative end of the same. Now, oppositely electrified bodies attract each other; therefore if we assume hydrogen to be endowed with positive electricity, it should be attracted towards the negative end or pole of the battery; and *vice versâ*, if we assume oxygen to be endowed with negative electricity, it should be attracted towards the positive pole or end. And this is what Davy imagined to be the case. He imagined all elements—and, indeed, all substances generally—capable of taking part in chemical combinations, to be endowed by nature with one definite kind of electricity; and that two molecules, or aggregates of molecules, having opposite electrical states, being brought in contact, under favourable conditions, would combine and form a chemical compound. Hence, according to this philosopher, chemical affinity is for molecules that which frictional electricity is for masses, a dual force, capable of penetrating matter, and each function of duality mutually attractive of the other. These premises being granted, it should follow conversely, that if electrical power of one definite strength accomplishes chemical union of particles, the application of electrical power, having greater strength, should separate those particles; and this is the explanation, according to Davy, of what occurs when water is decomposed, oxygen being attracted to the positive pole with a stronger attraction than that exercised by the associated hydrogen, and *vice versâ*.

Extending these decomposing effects of voltaic energy to various chemical compounds, it was found that metals—inflammable substances in general—the alkalies, earths, and oxides of the common metals, were liberated at the negative pole; whilst

oxygen, chlorine, and the acids, went over to the opposite extremity. It was, moreover, observed that the pole or extremity from which an element or a compound was liberated from one combination, was the same for all.

During a modification of these experiments it was that Sir H. Davy made his discoveries relative to the bodily transference of certain materials when exposed to voltaic decomposition. He commenced these investigations by trying what would be the result of connecting two glasses containing water, by some capillary substance, such as amianthus, and subjecting the water in either glass to voltaic agency.

Under these circumstances he found that decomposition ensued as before—oxygen gas appearing at the positive end, and hydrogen gas at the other. He next varied the experiment thus:—To the negative cup a solution of sulphate of potash or soda was poured, and into the positive cup distilled water; both cups were now connected by means of some filaments of amianthus, and voltaic electricity passed. Under these circumstances the liquid in the negative cup became alkaline, and the liquid in the positive cup acid. When the original disposition of liquids was reversed, the saline solution being contained in the negative cup, and water in the positive, the same ultimate result occurred. Again, mutual transfer was effected when distilled water was poured into the two terminal cups, and a saline solution in the middle or interposed cup, the three cups being connected by moistened amianthus.

But the most extraordinary phenomenon in relation to the voltaic transfer of bodies noticed by Davy was the transmission of one body through another, the two possessing a mutual affinity without combination; as, for example, the passage of an acid through a free alkaline solution, or the reverse. The three cups being arranged as before, a solution of sulphate of potash was poured into the negative cup, distilled water into the positive cup, and a weak solution of ammonia into the cup between, in such a manner that no sulphuric acid could arrive at +, without permeating the interposed ammoniacal liquor. Dispositions being as thus stated, and the battery being put into activity, free acid appeared at the positive pole. In like manner, hydrochloric and nitric acids were caused to pass through strong alkaline solutions; and, reversing the conditions, alkalies were transmitted through acids.

It is impossible not to associate the idea of attraction with the results detailed in the previous experiments; and, accordingly, the electro-chemical theory of Davy assumed electrical attraction of molecules to be identified with affinity. He assumed the total dual influence of the voltaic pile to be concentrated in its two ends or poles, and arrived at the conclusion that all compounds might be resolved into successive binary groupings, by exposing them to the influence of sufficiently powerful voltaic attraction. The theory is simple and fascinating; it is based on extensive observations and large generalizations; it cannot, however, be accepted to the full extent claimed by Davy, for reasons to be mentioned hereafter. Nevertheless, despite all modifications which this theory has received at various hands, it contains within itself an amount of verisimilitude, if not actual truth, incompatible with its total rejection. Modified in some form or other, it has been adopted by all chemical philosophers since the time of Davy, and still affords a means of classifying chemical bodies into *electro-positives* and *electro-negatives*.

Philosophers now agree that the decomposition of chemical compounds by the voltaic battery is not caused by polar attractions; that the appellation, pole, as applied to the metallic terminals of a voltaic combination, involves false views, and that the transmission, by voltaic influence, of acids across alkalies, and *vice versâ*, follows as a necessary consequence of the affinity between the two. For a determination of these facts, we are indebted to Professor Faraday.

Faraday's Modifications of the Polar Theory of Voltaic Combinations.—Supposing the electro-chemical theory of Davy to be a true representation of facts, every body, whether simple or compound, should either possess or have the tendency to assume one invariable quality of electricity. Hydrogen, and all bodies which, when separated by voltaic agency from their compounds, go to the negative pole of a voltaic arrangement, should either possess or have the tendency of assuming positive electricity. Oxygen, on the other hand, and other bodies termed electro-negative, because of their going to the positive pole, should be endowed with the opposite characteristic.

If bodies were naturally endowed with different kinds of electricity, the circumstance should admit of easy proof. We might appeal to the electrometer for demonstration; or, more pertinently still, we might appeal to the voltaic battery itself; for if a simple body, minutely divided, be suspended in some indifferent fluid, and voltaic electricity caused to traverse the fluid, the suspended particles should be attracted to one pole or the other. This is not the case. The experiment has been tried with charcoal minutely divided and held in suspension by sulphuric acid; it has been tried on gold precipitated by sulphate of iron from its solution, without the slightest positive effect. The greater number of bodies do not admit of this kind of experiment; but applying to them the analogy of others to which they are allied, it would seem that the theory which assumes molecules to be endowed with definite electrical states, is unfounded.

But this was not Davy's assumption. His theory did not require so extreme an admission, but would be substantiated in all that relates to the voltaic decomposition of bodies, on the assumption that a definite electrical state would be assumed by contact; and this postulate, judging from the investigations of himself and others, seemed to be granted. Volta, as we have already seen, referred the source of energy of combinations, which bear his name, to the contact of metals. Davy agreed with Volta in considering metallic contact the first cause of voltaic excitement, but he believed chemical action necessary to the sustaining of this excitement. That chemical action originated electricity, he strongly denied;* but Becquerel, Delarive, and Pouillet, have demonstrated the contrary.†

Volta's experiments on the development of electricity by contact had only extended to metals; Davy's investigations were more discursive, involving an examination of the electrical results of contact between various other bodies. He arrived at the conclusion that a dry alkali, or alkaline earth, is excited positively by contact with a metal, and that dry acids, after having been brought in contact with a metal, are negative. He satisfied himself, moreover, that acids and alkalies, in their dry state, mutually excite each other; the former assuming a negative, the latter a positive condition. Having satisfied himself on these points, he assumed that what was true for masses was true for molecules; and these postulates being granted, the reason why certain compound bodies were decomposed by voltaic power was thought to be satisfactorily explained.

Supposing, for the sake of discussion, every point to be conceded that was assumed

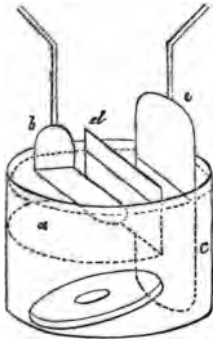
* "Bakerian Lecture," for 1836. † "Ann. de Chim. et de Phys." tome 25, 26, 27, 28, and 29.

by Davy, great difficulties present themselves, nevertheless, when the theory is applied to actual phenomena. It should follow, if the theory held good, that the affinity of one chemical compound for another must be less than the affinity of elements entering into these compounds for each other. Thus, for example, sulphuric acid is a compound of sulphur and oxygen; potash, a compound of potassium and oxygen—oxygen and sulphur, oxygen and potassium uniting in these cases, because either element is naturally in an electrical condition, opposed to that of the other. But if the electrical similitude invoked be fully borne out, the two electricities, by thus combining, should have mutually neutralized each other; whereas the potash and the sulphuric acid manifest a violent tendency to unite and form a second compound. Supposing the last objection to be removed, there is yet another. If the components of a substance be attracted towards either pole of a battery, they ought, according to every electrical analogy, to stay there. Supposing, for example, the decomposition of water to be that under consideration—hydrogen we know is liberated at the negative, oxygen at the positive pole. But this result should not ensue if the theory of Davy were correct. The hydrogen should not quit the negative, nor the oxygen the positive pole; but this is contrary to what takes place.

But the theories of Davy and Volta are based on a *petitio principii* which cannot be unconditionally granted; against which, indeed, there is a preponderating balance of testimony—the development of electricity by simple metallic contact. Delarive attributes the phenomena to slight oxidation,* and states that if the experiment be performed in an atmosphere of hydrogen or nitrogen, no electricity is developed. Professor Pfaff, of Kiell, cannot, on the other hand, subscribe to this statement; and Parrot, of St. Petersburgh, accepting the results, attributes them to friction.†

Struck with these inconsistences of Davy's theory, Professor Faraday undertook a lengthened investigation of the theory of chemico-chemical agency, and arrived at certain results which we may now investigate.

The first question which this philosopher proposed to himself for determination was this:—Whether voltaic decomposition was effected in consequence of polar attraction from without, or molecular divergence from within. To which question the following experiment afforded a satisfactory answer for one special case:—



"A glass basin, four inches in diameter, and four inches deep, had a division of mica (*a*) fixed across the upper part, so as to descend one inch and a half below the edge, and be perfectly water-tight at the sides; a plate of platinum (*b*) three inches wide was put into the basin, on one side of the division *a*, and retained there by a glass block below, so that any gas produced by it in a future stage of the experiment should not ascend beyond the mica, and cause currents in the liquid on that side. A strong solution of sulphate of magnesia was carefully poured, without splashing, into the basin, until it rose a little above the lower edge of the mica division (*a*), great care being taken that the glass or mica on the unoccupied or *c* side of the division in the figure should not be moistened by agitation of the solution above the level to which it rose. A thin piece of clean cork, well wetted in distilled water, was then carefully and lightly placed on the solution at the

* "Ann. de Chim. et de Phys." xxxix., p. 297. † "Ann. de Chim. et de Phys.," xlvi., p. 361.

c side, and distilled water poured gently on to it until a stratum, the eighth of an inch in thickness, appeared over the sulphate of magnesia; all was then left for a few minutes, that any solution adhering to the cork might sink away from it, or be removed by the water, on which it now floated; and then more distilled water was added in a similar manner, until it reached nearly to the top of the glass. In this way, the solution of the sulphate occupied the lower part of the glass, and also the upper on the right-hand side of the mica; but on the left-hand side of the division a stratum of water from *c* to *d*, one inch and a half in depth, reposed upon it, the two presenting, when looked through horizontally, a comparatively definite plane of contact. A second platinum pole (*e*) was arranged so as to be just under the surface of the water, in a position nearly horizontal, a little inclination being given to it, that gas evolved during decomposition might escape. The part immersed was three inches and a half long by one inch wide, and about seven-eights of an inch of water intervened between it and the solution of sulphate of magnesia.

The latter pole, *e*, was now connected with the negative end of a voltaic battery, of forty pairs of plates, four inches square; whilst the former pole, *b*, was connected with the positive end. There was action and gas evolved at both poles; but from the intervention of pure water, the decomposition was very feeble compared to what the battery would have effected in a uniform solution. After a little while (less than a minute), magnesia also appeared at the negative side: *it did not make its appearance at the negative metallic pole, but in the water;* at the plane where the solution and the water met.*

The platinum slip *c* being in contact with the saline solution, and the slip *a* with water,—then, supposing the theory of voltaic decomposition from polar attraction to apply, the results of decomposition (acid and magnesia) in this experiment should be attracted to either pole or slip of platinum. This view was not borne out in the result, as we have seen; but sulphate of magnesia suffering decomposition into its components, the latter were not attracted to the metallic slips or poles, but were deposited, or rather *imparted*, at the surface of contact between the water and the saline solution. The experiment just detailed is at variance with the assumption that decomposition follows as the result of polar influence exercised from without: it rather points to the existence of some molecular disturbance within the body decomposed. Further experiments substantiating the view thus taken, Faraday suggested the propriety of abandoning the words *attractive pole*, together with its necessary concomitants, and the introduction of others less expressive of a theory proved to be untenable. Hitherto the term pole having been used as synonymous with the effective end of the voltaic battery, and such effective ends having been metallic, experimenters lost sight of the fact that, however convenient the employment of metals for this purpose might be under all usual circumstances, nevertheless, supposing it desired to test a principle, fluids, and even gases, might be made the effective end; in which case, they would be analogous in function to the so-called metallic poles. An example of two liquids assuming this function, under a particular disposition of parts, is supplied by the last experiment; the demonstration, by another modification, can also be extended to gases.

Repudiating the idea of attraction as at variance with his experiments, Faraday arrived at the conclusion that the acting terminals of a voltaic battery, whether metallic, as in practice is usually the case, or fluid or gas, are not to be considered as localities of attraction, but as openings or doorways through which the electric current

* "Faraday's Electrical Researches," vol. i., p. 140.

enters, or issues, in its course. It was, therefore, desirable to adopt two appellations significant of the point of exit and the point of entrance of electricity. The former Professor Faraday denominated *anode* (ανα, upwards; οδος, way—*i. e.*, the course pursued by the rising sun), the latter *cat*—or, for euphony, *cathode* (κατα, downwards). Hence anode may be regarded as synonymous with *positive pole*, and *vice versâ*. The adoption of these terms led to others. It was clearly improper to retain terms expressive of attraction after repudiating the attractive influence; hence Professor Faraday, instead of denominating the results of voltaic decomposition electro-positives and electro-negatives, termed them *anions* and *cathions*, terms merely expressing the circumstance of their *going* to the anode or cathode. Hence, in general terms, *anion* and *electro-negative*, *cathion* and *electro-positive*, may be regarded as synonymous. Finally, the term electrolysis was introduced as expressive of voltaic decomposition; and all compounds amenable to such decomposition by direct influence of the battery are termed electrolytes. Between the direct and indirect decomposing agency of the voltaic battery it is necessary to make a distinction.

From a consideration of the modifications effected by Faraday on the theory of electro-chemical decompositions, it will be recognised that the main point insisted on by this philosopher is the existence of an internal divellent power between the molecules of compounds exposed to voltaic agency—a divellent power called into action by the voltaic influence, and determining a separation of molecules towards either electrode. Now this is just what takes places within the voltaic combination itself—indeed, perhaps the best general idea that can be given of the doctrine of Professor Faraday is to state that he regards the substance undergoing electrolysis, or decomposition, as a portion of the battery; whereas all philosophers anterior to him regarded them as extraneous to the battery.

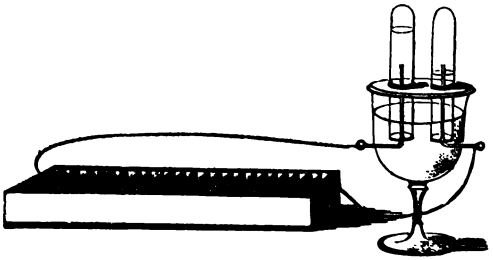
The acceptance of Davy's theory leads to the belief that the facility with which any compound admits of voltaic decomposition is in direct ratio to the weakness of combining force between the elements of such compound. Faraday's theory, however, leads to the directly opposite conclusion. According to it, bodies united by the strongest affinities should be most readily decomposed. So far as experiment has gone, the latter hypothesis seems borne out. Bodies formed of a binary arrangement of atoms may be assumed to possess the maximum of chemical stability; and, accordingly, Faraday discovers protoxides, protochlorides, &c., to be true electrolytes,—but extending his investigations to compound binary arrangements, such as metallic salts, the latter did not seem to come within the same generalization. However, further experiment will be needed to settle definitely the existence or non-existence of such analogy.

Chemical Proportionality of Voltaic Decomposition.—The view taken of voltaic chemical decomposition, and which has just been explained, has led to the important discovery that there exists an equivalent proportionality between chemical results and voltaic energy. For example, if two electrolytes or bodies capable of direct decomposition by voltaic energy be electrolysed by inclusion within the circuit of a battery, then each will be decomposed, and the quantities thus decomposed will be represented by the natural atomic weights of the bodies. Limiting this doctrine, for the sake of ready comprehension, to one specific case—that of the simultaneous decomposition of water and of chloride of silver fused—then for every eight parts by weight of oxygen, and one part by weight of hydrogen liberated, there will be 108 parts by weight of silver, and 35·45 of chlorine; such being the equivalent or combining weights of these bodies.

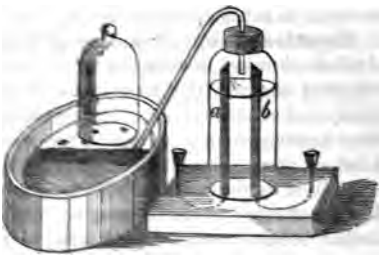
Again, if the same current be transmitted through four decomposing cells—the first of which contains water, the second chloride of silver, the third chloride of lead, the fourth chloride of tin, all fluid, the quantities of hydrogen gas, silver, lead, and tin precipitated at the four negative poles, are to each other as 1 : 108 : 103·6 : 57·9; whilst at the positive poles, oxygen and chlorine are separated in the proportions of 8 : 35·4.

Moreover, inasmuch as the doctrine of electrolysis, in contradistinction to that of electro-voltaic attraction, refers the voltaic decomposition of bodies to the exercise of forces residing within themselves, and, as a consequence, regards them as constituting an active portion of the voltaic circuit, the deduction would seem to follow that the total amount of chemical energy of one kind—whether a formation or resolution—brought into operation on one side of the voltaic battery, should be equal to that evolved on the other side—understanding by the term sides of a battery, the battery itself, ordinarily so called, and the substance placed within its circuit for the purpose of decomposition.

Thus, in the annexed woodcut, the two sides of a voltaic combination may be said to be, firstly, the battery itself; secondly, the water undergoing decompositon; and it is found that the total quantity of zinc dissolved in the battery proper is proportionate with the amount of water decomposed; that is to say, for every nine parts, by weight, of water decomposed, liberating eight parts of oxygen and one part of hydrogen, there will have been forty-six parts of oxide of zinc generated, and eighty-six parts of sulphate of zinc; such being the relative atomic weights of these substances. It is hardly necessary to indicate that, for the sake of precision, the battery is supposed to have zinc for its dissolving metal, and sulphuric acid for its dissolving agent.



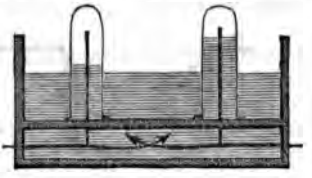
The application of this doctrine becomes of great theoretical importance in operations of electro deposition. A workman desires, for instance, to throw down, on a copper or other surface, a certain weight of gold or silver; he knows when this has been accomplished by simply measuring the amount of water decomposed by the same electric current. For accomplishing determinations, an instrument called the *voltameter* is employed. It is merely an instrument conveniently arranged for the decomposition of water by voltaic energy.



The accompanying woodcut represents a voltameter liberating its gases into a collecting jar placed over the pneumatic trough; *a b* are broad platinum electrodes, communicating respectively with either end of a battery.

I have already adverted to the curious phenomena of transference of certain bodies, under the influence of voltaic energy, through other bodies with which they ordinarily combine; but a far simpler case affords abundant matter for speculation.

Reverting to the ordinary electrolysis of water, we find that employing an apparatus like that of which a section is given in the woodcut, one electrode liberates hydrogen, the other oxygen.



Where then, at one exact point, does the decomposition of each atom of water take place? The advocates of a polar theory of decomposition reply to this question, it is true; but the reply involves a still greater difficulty. According to this polar theory, the decomposition must ensue at the attracting poles; namely, in the case under consideration, the sheets of platinum; but, inasmuch as one pole only liberates one gas, the difficulty arises of accounting for the transference of the other gas in an invisible form to the other pole.

Among the numerous theories framed with a view to explain this difficulty, that of Grotthus was most rational. He assumed that the water might be considered as forming a line of continuous binary particles between the two poles—something in the manner represented by Fig. 1—that decomposition occurred simultaneously at both ends of the line; but that the voltaic action was not maintained by the invisible crossing of oxygen and hydrogen. He explained the result more simply by assuming that the original disposition, as between molecules of oxygen and hydrogen, was brought about by molecular adjustment within the sphere of their own chemical attraction.

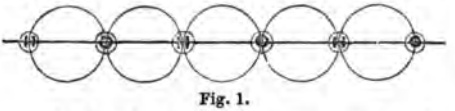


Fig. 1.

Fig. 2.

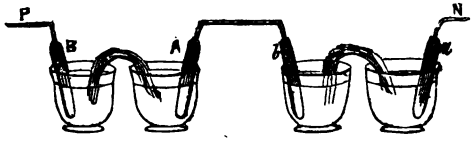
Then, referring to Fig. 1, it will be seen that if we take away the terminal particle of hydrogen from the left hand, and the terminal particle of oxygen from the right hand of the series, the elements of water will still remain, though not under the same polar arrangement as before; in order to restore which, the particles must be assumed to turn in their own sphere of chemical attraction, either to the right or to the left, as indicated in Fig. 2, when the original polarity would be assumed.

Now it will be seen that this theory may be applied to all cases of voltaic decomposition. Given the condition of chemical affinity between two bodies, such as oxygen for hydrogen, or sulphuric acid for potash, &c., and the theory of molecular adjustment is rational; but without that condition the theory does not apply. Hence, the transmission of soda through sulphuric acid, or sulphuric acid through soda, and similar results which appeared so extraordinary to Davy, because of the strong chemical affinity existing between the two, should take place according to the theory of Grotthus, because of that affinity, and should not be capable of taking place without. Although such a deduction naturally flows from the theory of Grotthus, yet it does not seem that that philosopher perceived them, and it remained for Faraday to point them out, and to demonstrate them by numerous satisfactory experiments; one of which is as follows:—

Two solutions having been prepared—one of sulphate of soda in water, the other of sulphuric acid in water—and the strength of the solutions having been adjusted in such

a manner that in a given number of volumes of sulphate of soda there should be contained the same amount of sulphuric acid as in an equal number of volumes of the aqueous solution of that acid, the experiment was proceeded with as follows :—

Four glass cups were arranged; seventeen measures of the free sulphuric acid were put into each of the vessels *a* and *b*, and seventeen measures of the solution of sulphate of soda into each of the vessels A and B, the portions being as equal as they could be made in quantity, and cut as short as was consistent with their performing the part of effectual communication. B and *a* were connected by two platinum plates or poles, soldered to the extremities of one wire, and the cups *a* and B were, by similar platinum plates, connected with a voltaic battery of forty pairs of plates, four inches square, that in *a* being connected with the negative, that in B with the positive pole.



The battery, which was not powerfully charged, was retained in communication above half an hour. In this manner it was certain that the same electric current had passed through *a b* and A B, and that in each instance the same quantity and strength of acid had been submitted to its action; but in one case merely dissolved in water, and in the other dissolved and also combined with an alkali.

On breaking the connexion with the battery the portions of asbestos were lifted out, and the drops hanging at the ends were allowed to fall each into its respective vessel. The acids in *a* and *b* were then first compared, for which purpose two evaporating dishes were balanced, and the acid from *a* put into one, and that from *b* into the other; but as one was a little heavier than the other, a small drop was transferred from the heavier to the lighter, and the two rendered equal in weight. Being neutralized by the addition of the soda solution (a solution of known and definite strength, each measure being equivalent to a measure of sulphuric acid), that from *a*, or the negative vessel, required 15 parts of the soda solution, and that from *b*, or the positive vessel, required 16·3 parts. That the sum of these is not 34 parts is principally due to the acid removed with the asbestos; but, taking the mean of 15·65 parts, it would appear that a twenty-fourth part of the acid originally in the vessel *a*, had passed through the influence of the electric current from *a* to *b*.

In comparing the difference of acid in A and B, the necessary equality of weight was considered as of no consequence, because the solution was at first neutral, and would not, therefore, affect the test liquids, and all the evolved acid would be in B, and the free alkali in A. The solution in A required 3·2 measures of the prepared acid to neutralize it, and the solution in B required also 3·2 measures of the soda solution to neutralize it. As the asbestos must have removed a little acid and alkali from the glasses, these quantities are by so much too small; and, therefore, it would appear that about a tenth of the acid originally in the vessel A had been transferred into B during the continuance of the electric action.*

* "Faraday's Experimental Researches in Electricity," vol. i., p. 152-3.

From the preceding experiment it appears that more acid was transferred from the saline solution than from the aqueous solution of acid,—a result at variance with the theory of mere electrical attraction. Sulphuric acid, as existing in sulphate of potash, could not have escaped before a certain force—namely, that of affinity—had been overcome; whereas, the force to be overcome in the second case was merely the affinity of sulphuric acid for water.

"Some of the most beautiful and surprising cases of electro-chemical decomposition and transfer," Professor Faraday remarks,* "which Sir H. Davy described in his celebrated paper,† were those in which acids were passed through alkalies, and alkalies or earths through acids; and the way in which substances having the most powerful attraction for each other were thus prevented from combining, or, as it is said, had their natural affinities destroyed or suspended throughout the whole of the circuit, excited the utmost astonishment. But if I be right in the view I have taken of the effects, it will appear that that which made the *wonder* is in fact the *essential condition* of transfer and decomposition."

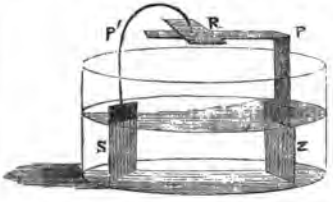
Theories of Voltaic Action.—Although some of these theories have already been casually noticed, yet it will be desirable to state them definitely, in close mutual apposition. Dismissing altogether the theory of Galvani, who referred the effects of voltaic energy to an animal origin, and considered the metals used only in the sense of conductors; dismissing also the theory of Fabroni, who denied electricity to be the cause of the phenomena noticed by Galvani—neither of which can be denominated theories of voltaic energy properly so called—the true theories of this agency may be classed under the binary division of those which refer the power to simple contact of metals as its source, and those which refer it to chemical action.

Volta, it has already been stated, adopted the former view, ignoring the chemical results of voltaic agency altogether, as casualties. This view of the case, however, was so obviously untenable that it was universally abandoned. A modification of the theory, however, was adopted by Davy; and indeed its adoption, thus modified, is a necessary postulate in the acceptance of Davy's electro-chemical theory. Fully admitting, with Volta, metallic contact to be the primary source of electric disturbance in voltaic arrangements, Davy believed that the restoration of equilibrium was alone brought about, and prolonged agency of the combination effected, by subsequent chemical decomposition. The theory is hence so intimately associated with the doctrine of electro-chemical decomposition, and has been discussed so fully under that head, that I need not further extend these remarks, referring the reader to pp. 248—250 for all further particulars on this subject.

Wollaston adopted a different view. He attributed all the electricity evolved to chemical action as its source, but did not follow this theory to its legitimate conclusion. The theory of Wollaston is now almost universally accepted. It is that which alone accords with the doctrine of electrolysis, and it is, moreover, supported by the almost insuperable argument, that voltaic combinations may be made without any metallic contact, and that, in all the most powerful voltaic combinations, no such direct contact does take place; the truth of which remark will be evident when the construction of voltaic arrangements shall be described. Slightly anticipating that part of the subject, the following experiment of Faraday may be appropriately cited in demonstration of the fact, that voltaic action, as evinced by chemical decomposition, may ensue without metallic contact.

* "Electrical Researches," vol. i. † "Phys. Jour.," 1807, p. 1.

If a piece of zinc and of silver be placed without contact in a vessel of dilute sulphuric acid, and joined by means of a wire, a simple voltaic arrangement will result.

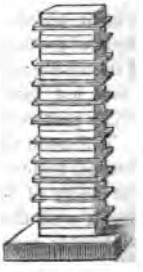


If the wire be now supposed to be broken in the middle, and a body such as R inserted between the two ends, it is evident that a voltaic current, supposing one to take place, will be favourably circumstanced for passing through R and decomposing it, if capable of decomposition. Now, if R be a disc of bibulous paper, filled with a solution of iodide of potassium and starch, and laid for convenience on the flattened platinum electrode P, as represented in the diagram, whilst its upper surface is touched with the platinum wire P', decomposition of the iodide of potassium ensues, as evidenced by the paper immediately turning blue. In this case it is evident there was no metallic contact.

Nevertheless, there are not wanting, especially among continental philosophers, advocates who still attribute a portion of the electricity evolved from active voltaic combination to metallic contact.*

The advocates of metallic contact as being partly the cause of voltaic energy, not only relied on the experiments relative to the development of electricity by metallic contact, already detailed, but on the phenomena of De Luc's electrical column, as the instrument is termed. It consists of a glass tube, in which are packed some thousand discs of paper, covered with silver on one side and zinc on the other. This instrument gives unequivocal electric indications; and it was argued that such indications are a proof that the electricity is developed by contact. Except, however, the zinc be protected from oxidation, the inference goes for nothing; and such protection is incompatible with the conditions of the instrument's construction.

Different Forms of Voltaic Combinations.—The first compound voltaic arrangement ever made was the pile; an instrument consisting of discs of copper and zinc, or other dissimilar metals intended to be used, soldered together, a piece of moistened flannel or card being interposed between each pair. To this form of apparatus the objections are numerous. Not only does the construction of such an arrangement occupy considerable time, but during construction there is also excitation; for which reason the power of the lower part of the apparatus is considerably diminished before the upper part comes into operation. Moreover, the quantity of fluid employed is limited: firstly, by the power of the flannel discs to absorb; secondly, by the downward pressure of the superimposed portions of the apparatus. The efficiency of the instrument is still further diminished by a lateral communication of liquid passing from plate to plate. To obviate these disadvantages, Mr. Cruickshank formed the voltaic or galvanic trough, which may be described as the voltaic pile, laid horizontally.

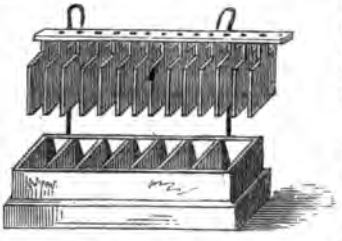


Cruickshank's instrument was formed by joining discs of the two metals

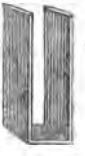
* On this subject consult Dr. Chr. M. Poulsen's inaugural dissertation, "Die contact theorie vertheidigt gegen Faraday's abhandlung über die Quelle der Kraft in der Volta'schen Säule." Heidelberg, 1845.

together, and inserting each compound disc within a trough, at right angles to its long axis, and water-tight, by which means the trough became separated by the compound discs into many compartments, each corresponding to the disc of moistened flannel in the original voltaic pile. The trough itself was usually made of wood, and coated internally with a layer of fused pitch or resin, which answered the double purpose of protecting the wood from the acid liquor employed, and of securing the metallic discs in their places, without permitting lateral communication to ensue.

The next form of voltaic battery adopted the principle of the *Couronne des Tasses*, and consisted of two parts,—namely, the trough or acid container, and the metallic combinations for dipping into this trough. The former is precisely similar, in general appearance, to the entire apparatus of Cruickshank, though its principle is entirely different—the transverse diaphragms not being metallic pairs, but of the same material as the trough—and this was usually of earthenware. The appended sectional diagram furnishes an idea of this instrument.

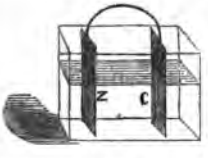


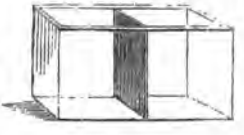
Dr. Wollaston it was, I believe, who next showed that the power of a voltaic battery might be greatly augmented by reduplicating the copper plate in the manner shown; hence arose a further modification of the battery: and from this idea of Wollaston, the proposition of discarding glass or porcelain cells altogether, and forming the copper part of a battery into cells, was an easy transition.



The original battery of Volta thus became greatly modified in form, and each modification exhibited an obvious improvement. One disadvantage, however, remained: the power of the arrangement was not constant. Professor Daniell obviated this inconvenience by devising his constant battery, the principles of which I shall now explain.

Starting with the consideration of a simple voltaic arrangement, as represented in the diagram, where a slip of zinc is connected by an intermediate wire to a slip of copper, and both are immersed in a vessel of dilute sulphuric acid, experience proves that, after the lapse of a certain period, the apparatus ceases to act: the limit to its action being partly the expenditure of acid, partly a deposition of zinc upon the copper plate—this resulting from a decomposition of oxide of zinc by hydrogen. If any modification of arrangement could effect the deposition of copper upon copper, and renew a supply of sulphuric acid, the result should be a constant battery.



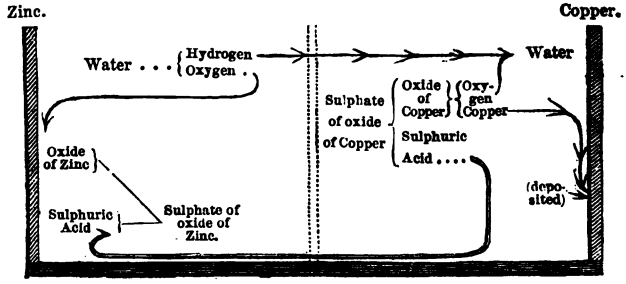


Let us now consider what the probable effect would be of dividing the glass vessel into two halves, by an interposed layer of membrane, a

diaphragm of plaster of Paris, or other convenient porous body barely admitting of permeation; and filling the copper cell, not with dilute sulphuric acid, as before, but with sulphate of copper. Under these new conditions, sulphate of copper and dilute acid would become electrodes mutually to each other; and the oxide of zinc, which, under former conditions, would have been deposited on the copper, would be now deposited at the plane of junction of the dilute acid with the sulphate of copper solution—*i. e.*, the diaphragm. Meantime, the electrical influence, passing on, would penetrate the sulphate of copper, and determine a deposition of *copper upon copper;* whilst the sulphuric acid of the decomposed sulphate of copper permeating the membrane, would pass into the original acid division of the apparatus, and compensate for that which had already been expended.

Supposing these theoretical indications verified (as they are), such a battery would be constant so long as fresh sulphate of copper was supplied, and while the materials of the battery lasted.

The rationale of such a battery is indicated by the subjoined diagram; and its constant action depends upon the circumstance, that the copper plate is always

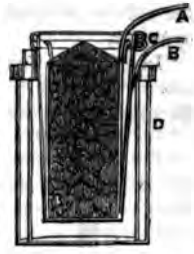


retained bright—having, in point of fact, deposited upon its surface a layer of the same metal from the decomposing solution of *sulphate* of copper. It follows, then, that if the original plate of copper were possessed of any inequalities of surface, the latter would be faithfully represented by the deposited layer of metal. In point of fact, this is the most elementary view that can be taken of the theory of electro-deposition, the simplest process of effecting which consists in making the subject to be copied an element of a simple voltaic arrangement. In this case, however, the subject to be copied must either be of copper, or of some metal possessing a similar voltaic energy in regard to zinc. Otherwise a compound voltaic arrangement must be employed, furnished with wires; and the subject to be copied must be attached to that wire which, adopting the language of theory, receives the electric current (cathode), and conducts it back to the battery.

These theoretical principles have been carried out in the constant batteries of Becquerel, Daniell, and Mullins; the arrangements being most perfect in the battery of Daniell, although the instruments of Becquerel and Mullins possess greater simplicity.

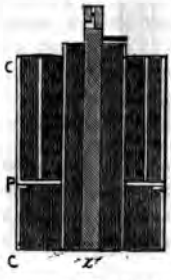
Mullins' battery consists of an earthenware trough, D, in which a cylindrical plate, B, of zinc, nearly equal to the trough in diameter, is placed. Within the zinc cylinder is

inclosed one of copper, A. A bladder is tied round the upper edge of the copper cylinder, C, into which fluid may be introduced by means of a row of apertures in the rim. The bladder is now filled with a solution of sulphate of copper, and coarsely pounded crystals of sulphate of copper are heaped upon the copper cylinder. The trough is now charged with sulphuric acid, which, coming in contact with the zinc, acts upon it in the ordinary way.



Daniell's constant battery is constructed upon the same general principles; but the mechanical arrangement of its parts is reversed—the copper being outside, the zinc inside—by which means the principle first noticed by Dr. Wollaston is taken advantage of; namely, that the copper surface of a battery should be greater than the associated zinc surface.

The accompanying diagram represents a section of Daniell's battery. The cell is composed of a copper cylinder, C C, towards the upper part of which a perforated plate, P, is situated, upon which, as a platform, crystals of sulphate of copper are laid. The zinc portion of the battery is a solid rod, *z*, supported above by a cross piece of wood, and separated from the copper cell by the membrane of a bullock's gullet.



Hitherto zinc and copper have been exclusively mentioned as the metals of which voltaic arrangements are formed: they are not theoretically the best, however; and in the construction of all our most powerful voltaic batteries the combination is departed from. Theoretically speaking, the battery of maximum power should consist of two solids and a fluid—one solid possessing the maximum, and the other the minimum power of affinity with that fluid. Hence, supposing the fluid to possess an oxidizing tendency, the best theoretical materials for constructing a battery should be potassium and platinum. Potassium is obviously out of the question; and, on examining the list subjoined, we find zinc to be the most oxidizable metal compatible with our resources:—

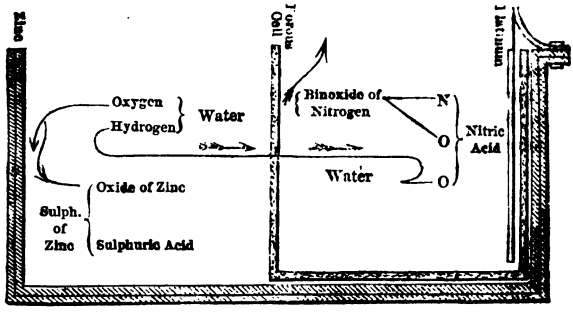
Platinum.	Copper.	Zinc.
Gold.	Tin.	Sodium.
Silver.	Lead.	Potassium.
Mercury.	Iron.	

Platinum, however, is *not* out of the question. Although expensive at first, it never wears out, and is, accordingly, employed in more than one form of powerful voltaic battery. The battery invented by Mr. Grove is of this kind; consisting of binary metallic arrangements of zinc and platinum, not both immersed in one fluid. Nitric acid is the fluid employed for contact with the platinum—dilute sulphuric acid, mixed with nitric acid, for contact with the zinc; and the two fluids are prevented coming in bodily contact by the intervention of a porous earthenware cell, into which the nitric acid is poured, the cell being immersed within the dilute sulphuric acid.

This battery is exceedingly powerful, but not very permanent; and the evolution of nitrous fumes which it occasions when worked for any considerable length of time is inconvenient; moreover, the fluid, after the lapse of a certain period, becomes heated even to ebullition. All these drawbacks limit the utility of the instrument; but for

developing vast amounts of voltaic electricity in limited time, and from a limited space, no other instrument is comparable with it. The accompanying diagram presents the scheme of decomposition which ensues within this battery when brought into operation.

In all voltaic batteries of which commercial zinc constitutes a part, a considerable amount of power is lost by the secondary currents which are set up on the surface of the zinc itself, in consequence of the impurities which the commercial metal contains.



If pure zinc be employed, these secondary currents do not occur; but pure zinc cannot be obtained at a price sufficiently low to admit of its being employed, hence some expedient had to be devised for increasing the efficiency of common zinc. This can be effected by amalgamation; accordingly, it is now usual to amalgamate all surfaces of common zinc which enter into the construction of voltaic batteries.

Amalgamation of zinc plates is readily effected by rubbing them, after being scoured, with a solution of nitrate of mercury in nitric acid. As soon as an even coating of mercury has been deposited, the plates should be dipped in water, to remove the adherent acid, and then placed to drain off the moisture.

Mr. Smee has invented a battery which, though not so powerful as the one just described, has perhaps a larger sphere of application. Instead of using platinum as in the above, the equivalent is silver, on which a superficial coating of platinum has been deposited. Bunsen substitutes carbon cylinders for the platinum or platinized silver; the form of carbon employed being that which results from strongly igniting a mixture of powdered coke and sugar. The materials are formed into shape by means of an iron mould, and afterwards burned.

MAGNETIC EFFECTS OF VOLTAIC ELECTRICITY.

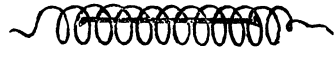
Electro-Magnetism.—At a very early period in the history of electrical science, the opinion prevailed that some connection subsisted between electricity and magnetism. Nor is it difficult to understand the reason of this opinion. Numerous cases are on record of the assumption of magnetic properties by pieces of iron and steel, originally *non*-magnetic, after having been struck by lightning. Numerous, however, as are these instances, the results themselves were capricious. For one case in which a piece of iron or steel was rendered magnetic by a flash of lightning, several occurred under

circumstances apparently similar in which no such consequence followed. Accordingly, the opinion at length began to prevail amongst philosophers, that the connection between lightning strokes and magnetic results did not stand in the relation of cause to effect—that it was a coincidence, and nothing more.

At this time, when the conditions of electro-magnetic phenomena are so well understood, it excites no wonder that the electrical experiments devised by philosophers for settling the question led to negative results. A vicious theory pervaded electrical as well as magnetic science, and paralyzed the power of investigation. The necessary function of duality, which the beautiful reasoning of Faraday has made an integral portion of electrical and magnetic study, was then unknown. Experimenters believed that either northness or southness in a magnet, or the condition of positive or negative, as regards electricity, might be capable each of an individual existence. Actuated by this doctrine they contented themselves with bringing successively each of the terminal ends, or, in conventional language, "poles," of a voltaic combination in close proximity with either end or pole of a magnet. But the magnetic extremities remained perfectly indifferent under this treatment. The north-pole was not attracted—the south-pole was not repelled—nor *vice versa*. Hence, the deduction was arrived at, that between electricity and magnetism there was no necessary connection whatever. As the direct consequence of such an experiment, the result could not be otherwise than we find it; but the wonder now is that the true conditions of electro-magnetic development should not have been discovered collaterally, or by accident. If, instead of bringing the extremity of each terminal wire of a voltaic arrangement successively near to either pole of a freely-suspended magnet, the two conducting wires of the voltaic arrangement had been made temporarily one, by contact, and the freely-suspended magnetic needle held somewhere in the vicinity of their track, then the secret reserved for the genius of Oersted to discover, in 1819, would have been anticipated by many years.

Notwithstanding that the first or accidental instances of communicated magnetism by electrical agency were the results of atmospheric electricity, which latter is analogous in its functions to frictional electricity, as produced by the machine, almost all of the electro-magnetic phenomena capable of being developed artificially require the aid of voltaic electricity. However, one very simple, and at the same time instructive, experiment of this kind admits of being performed by means of the frictional machine; and I think it desirable to mention it at once, inasmuch as it serves to create a true notion of electro-magnetic action in general. The experiment is as follows:—

Having procured some copper or brass wire, wind it round a stick or ruler in such a manner that, on slipping out the latter, the wire may remain in the form of a helix. Next take a sewing-needle, envelop it in paper (an imperfect conductor), lay the needle, prepared as described, in the helix, and transmit through the whole length of wire constituting the latter, the charge of a Leyden jar. On now removing the needle, and testing each extremity in the usual manner by means of a suspended magnet, the needle will be found to have become magnetic; indeed, so strongly magnetic is it usually, that by its attraction small filaments of iron may be raised.



Now, the experiment in question is not capricious. Given the necessary conditions, and the result is always the same: hence, even without an appeal to voltaic combinations, by means of which alone all the more important electro-magnetic experiments are capable of being performed, the electrical influence of a common Leyden jar suffices

to prove, contrary to the opinion of some electricians before the time of Oersted's discovery, that some real connection exists between electricity and magnetism.

A little reflection will prove that, in the experiment just described, the magnetic polarity has been developed at right angles to the helical axis of the copper wire: at right angles, in other words, to the general current of electricity passing through the wire. Now this is universal—no matter how varied or how complex the electro-magnetic arrangement may be; and a remembrance of the fact is an essential point in all electro-magnetic studies. The proposition, reduced to its simplest expression, is this: "*All electric currents have a tendency to impart magnetic agency to all neighbouring bodies.*" It so happens that iron and steel are easily affected by this influence; and hence the needle is converted into a magnet.

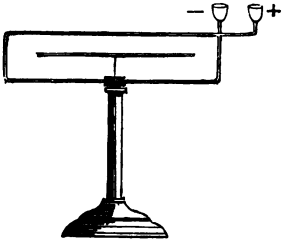
The memorable experiment of Professor Oersted, from the period of which the science of electro-magnetism dates its origin, was of this kind:—The ends of a voltaic battery having been connected by means of a terminal wire, so that the current of electricity—to use the language of theory—was transmitted from one end to the other, and a freely-suspended magnetic needle having been brought near to this wire, the needle became affected with all manner of irregular movements. When the wire was placed above the magnet, and in parallelism with it, the pole corresponding with the negative end of the battery always moved westward. When the wire was placed under the needle, the same pole invariably went eastward. When the wire was placed on the same horizontal plane with the needle, the magnet tried to assume a vertical movement; the pole next to the negative side of the battery dipping when the wire was to the west of it, rising when the wire was placed to its east side.

Doubtless, the student will think all these movements complex and irregular, as, indeed, did M. Oersted, and all the earlier electro-magnetic philosophers. There is a very easy means, however, of reducing them to lucid order. It is as follows:—Let the theory of one electric fluid be adopted; let us agree to call the end of the voltaic arrangement from which the electric current sets out on its course, positive, and the other end negative: next, let the student imagine himself to be an electric conductor, capable of transmitting the electric current, which must be furthermore assumed to pass from the direction of his head to his feet; then supposing him to hold a magnet in his hand, directly in front, and the north pole of the magnet pointed towards the head—then, all these conditions being complied with, if a current of electricity be passed in the direction indicated, the north pole of the magnet will point to the right hand.

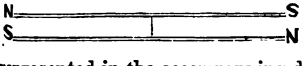
Any means which exist for impressing directive notions, so apparently complex as are those of a magnetic needle under the influence of an electric current, on the memory, may be with propriety adopted, even though the apparatus of illustration should be a toy. I would advise the student, therefore, who is desirous of analyzing the apparently complex motions of magnetic needles with facility, to prepare a toy of the following description:—Cut the representation of a soldier out of cork or wood; arm him with a musket and bayonet. Assume the musket and bayonet together to be a magnet, of which the bayonet is the north pole. Assuming, furthermore, that a current of electricity passes through the soldier in the direction from head to heels, then the bayonet should always turn to the right hand. If the student will take the trouble to construct the original arrangement of Professor Oersted, and test the appa-

rently anomalous movements noticed by that philosopher, he will find them all to be strictly accordant with the directive tendency of the magnet, as illustrated by the toy soldier. It is to be remarked that in both Oersted's experiment, and the experiment with the sewing needle and wire helix, the magnetic phenomena are the result of electricity in motion. This circumstance is universal; static electricity, or electricity at rest, produces no magnetic effects whatever. Another peculiar characteristic of electro-magnetic phenomena is that the influence takes place across non-conducting materials. The influence of Oersted's uniting wire takes effect through plates of glass, wood, metal, and the resinous plate of an electrophorus.

The Galvanometer.—It has been said that the tendency of an electric current is to cause a freely suspended magnetic needle in its vicinity to assume a position of final rest at right angles to the former. The exact amount of deflection, however, is proportionate to the strength of the voltaic battery. Far more valuable, however, is the indication of directive tendency which a magnetic needle discloses: it proclaims the direction in which the electric current is passing; or, to avoid the language of theory, it shows practically the direction in which + and — electricity are respectively developed. A single wire, as in Oersted's original experiments, will serve to indicate this; but if the wire be made to surround the needle, the effect is still more marked. An instrument of this kind is represented in the accompanying diagram, and constitutes the galvanometer in the simplest form the instrument can assume.



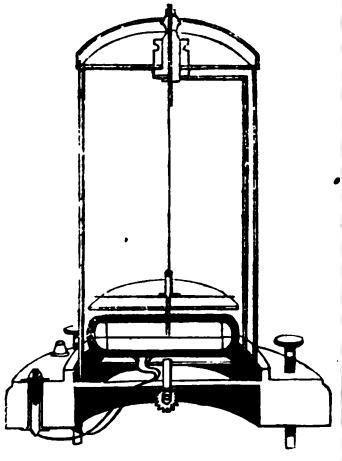
We are indebted to Schweigger for discovering a means of enormously increasing the delicacy of this instrument. This philosopher proved that the amount of deflection was proportionate to the total number of insulated coils of which the rectangle might be formed; hence the most sensitive galvanometers are those which are constructed on this principle. I have hitherto assumed that a simple magnetic needle has been employed in the experiments; but reflection will manifest that such a needle not only responds to the artificial influence determined by electricity, but to the primary influence of terrestrial magnetism. When, therefore, it is desired to render the galvanometer as delicate as possible, a compound magnetic needle, termed *astatic*, is employed. A compound or astatic magnetic needle is constituted of two simple needles of equal strength, separated slightly from each other, and the north pole of one exactly opposite the south pole of the second, as it is represented in the accompanying diagram.

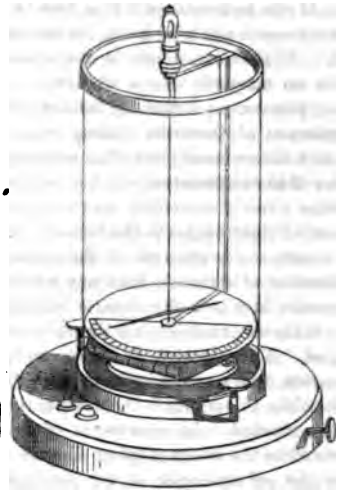


Such a combination as the one now described would have no directive tendency whatever as regards the earth's magnetic influence; but it would be nevertheless amenable to the influence of an electric current. Practically, however, it is found desirable to have one of the magnets *a little* stronger than the other, by which provision it retains sufficient directive tendency to place itself north and south, but not enough to interfere seriously with the indications of the electric current.

The diagram given on the following page represents a galvanometer in its most approved form. For the purpose of isolating the instrument from passing currents, and other causes of interference, it is protected by a glass shade; and the torsion

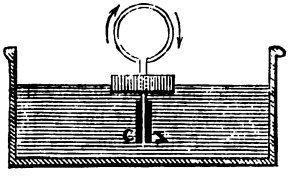
of a silken filament, as in the torsion electrometer already described, is employed as a restraining force.





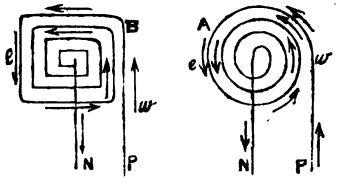
The influence of a wire conducting electricity on a freely suspended magnet is suggestive of the idea that the conductor itself is, whilst in action, also magnetic; and the truth of this assertion was demonstrated almost at the same time by Davy and Arago. So strongly magnetic, indeed, is it susceptible of becoming, that its power of lifting iron filings is considerable. Moreover, various forms of apparatus admit of being constructed to illustrate the directive tendency of such wire magnets. Of this kind are the following:—

A circular copper wire, having its extremities passed through a cork, and to one extremity soldered a small plate of zinc; to the other, a small plate of copper. The arrangement, as will be seen, constitutes a simple floating voltaic combination. It can readily be excited by floating it in dilute sulphuric acid, and will, of course, be free to assume any directive tendency. On causing either pole of a magnet to approach this little apparatus on different sides, the floating combination will manifest various phenomena of attraction and repulsion, all explicable on the principles already enunciated. The instrument admits of being rendered still more delicate by covering the wire with some non-conducting substance, and reduplicating the number of turns on the principle of the improved galvanometer. Such an improved instrument is represented on the following page.

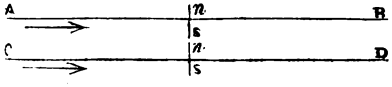


The magnetic characters of wires in the act of transmitting electric currents may be also readily demonstrated by means of forms devised by Ampère, and represented in the following cut. The forms of apparatus in question may be delicately suspended or converted by means of pieces of cork and metallic plates into floating arrange-

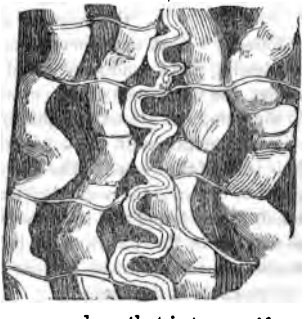
ments, similar in principle to the one described in the present number. Thus arranged, the flat spirals will always arrange themselves in the direction of north and south; one definite side of the coil always corresponding to one invariable direction of the electric current. In conformity with principles already enunciated, each coil of the flat helices may be regarded as a separate magnetic pole; therefore it will readily be seen, that in proportion as the number of coils is increased, so in equal measure will be the amount of directive tendency.



Mutual Effects of Parallel Electric Currents.—We have seen, under the head of electricity considered as a static force, that is to say considered as at rest, that two similarly electrified bodies are mutually repulsive of each other; it now remains to examine the mutual influence of electrical currents on conducting bodies which transmit them. The simplest case is that of parallel electric currents, the result of passing electricity through which, in the same direction, is mutual attraction. The reason of this will be seen on examination of the following simple illustration, in which the left sides of the wires A B and C D respectively assume a north magnetic polarity, and the corresponding right sides a south magnetic polarity. The left and right handedness are obviously determined by reference to the direction of the passing electrical current, indicated in the diagram above by the arrows. Now it is accordant with one of the first laws of magnetism that the opposite poles of any two magnets should be mutually attractive; hence the two wires performing the functions above represented would approach each other.



The result in question has been made the basis of a philosophical theory—the theory of muscular contraction of MM. Prevost and Dumas, and it at least is more satisfactory than several others which have been adduced in explanation of the phenomenon. Certain postulates must be granted before the electro-magnetic theory of muscular contraction can be accepted. Electricity must be assumed as identical with nervous energy. The nerves distributed to muscular tissue must be assumed to diverge in parallel lines at right angles to the muscular tissue. Granted the above postulates—granted the existence of an arrangement of nerves and muscular filaments, as represented in the diagram annexed—granting the transmission of electricity as shown in the engraving, it is evident that the muscular tissue should contract.

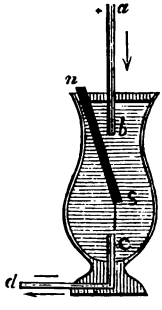


It is scarcely necessary to indicate the fact, that if two wires, near together, parallel to each other, and free to move, have electricity directed through them in a parallel direction, though in reverse order—that is to say, if one wire be made to transmit a current of electricity from right to left, whilst the second is made to transmit it in the direction from left to right—repulsion will be the conse-

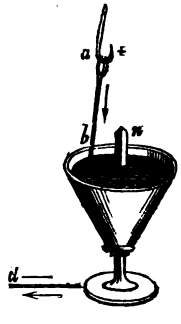
quence; neither will it be desirable to investigate the numerous phenomena which can be made to manifest themselves, under the circumstances of the employment of two or more conducting wires near to each other on various aspects. Suffice it to remark, that in this, as in every other instance of the co-operation of numerous mechanical forces, the effect is referable to a mean resultant of the whole.

We have hitherto seen an electric current manifesting different magnetic powers under different aspects. When first remarked, these varying influences appear very complex. We may contrive, by means of a *memoria technica*, to systematise them, but they admit of still further simplification. Referring to the experiment described at page 263, it will be seen that the strongest possible similarity subsists between a spiral wire, conducting electricity, and a magnet; therefore an idea is at once suggested that electro-magnetism is a spiral, or rather a tangential force. This view of the subject removes many difficulties. At the period of the original discovery of Oersted, and for some time subsequently, the idea prevailed that a force at one time attractive, and at another time repulsive, acted in straight lines between the magnet and the conducting wire. The opinion soon afterwards began to gain ground, that such numerous attractions and repulsions, ever varying, were more nearly suggestive of rotation. A well-devised experiment of Professor Faraday soon brought the opinion to the test, and settled the point affirmatively. The experiment was as follows:—

A glass cup had its bottom perforated, and through the perforation was let the conducting wire, *d* C. To this the south pole of a magnetic bar, *n* S, was attached by means of a piece of thread, and the cup being filled with mercury, the magnetic bar of course floated. The conductor *a b* was now caused to dip into the mercury, and a current of electricity transmitted along the conductor in the direction of the arrow, so that the current entered at *a*, and emerged at *d*. No sooner was electrical connection established than the magnetic bar commenced rotating around the bar *a b*. So long as the electric current descended in accordance with the diagram, the north-pole of the magnetic bar remaining upwards, the latter rotated round the wire *a b*, passing from east to south exactly like the movements of the hands of a watch; but, on causing the electric current to ascend, the direction of the magnet was changed.



Faraday's next experiment was made for the purpose of demonstrating that a conductor would rotate around a magnet. A magnet, the north-pole of which, *n*, is represented uppermost in the diagram, was placed upright in a cup full of mercury, and in communication with the conducting wire *d*, running through the bottom of the vessel. The moveable conductor *a b* was then caused to dip into the mercury, and an electric current being passed, it was found that the moveable conductor rotated around the magnet in the direction of left to right, or right to left, according as the electrical current was caused to pass upwards or downwards in the series.

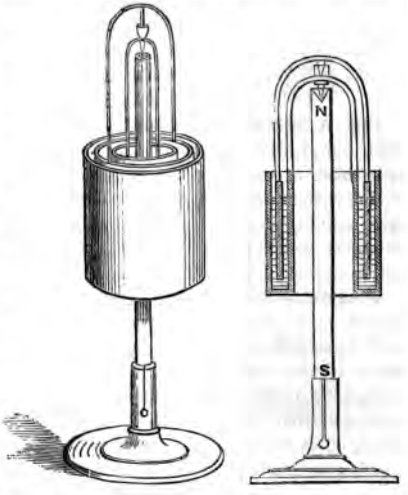


By means of these and similar experiments, it is demonstrated that a magnet is inclined to rotate in a plane perpendicular to the electric current which influences it; and this result is most simply explained by assuming the operation of a force

acting upon the pole at every point of its course tangentially to the circle in which it moves.

By using a delicate apparatus, the magnetic pole of the earth may be made to put the wire in motion. The rotation then takes place around a line parallel to the dipping needle; hence the rotatory wire must always be inclined, so that the solid it describes in revolving, if a cone and not a mere circle, should include a line parallel to the dip which passes through its apex.

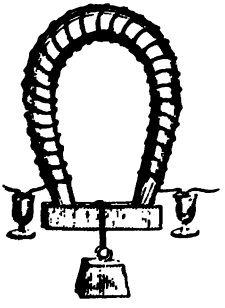
Another ingenious contrivance for illustrating the rotatory motion of the wire round the pole of a magnet, has been invented by M. Ampère, and has the advantage of comprising within itself the voltaic combination which is employed. It consists of a cylinder of copper about two inches high, and an inch and three-quarters internal diameter, having within a smaller cylinder about one inch in diameter.



The two cylinders are fixed together by the larger having a hole cut in its centre from below, the size of the smaller cylinder, leaving a circular cell, which may be filled with acid. A piece of strong copper wire is fastened across the top of the inner cylinder, and from the middle of it rises, at a right angle, a piece of copper wire, supporting a very small metal cup, containing a few globules of mercury. A cylinder of zinc, open at each end, and about one and a-half inch in diameter, completes the voltaic combination. To the latter cylinder a wire, bent like an inverted U, is soldered at opposite sides; and in the bend of this wire a metallic point is fixed which, when fitted in the little cup of mercury, suspends the zinc cylinder in the cell, and allows a free circular motion. An addition to this apparatus was suggested by Mr. Barlow, and constructed by Mr. Newman, who fixed an additional point, directed downward from the central part of the stronger wire, which point is adapted to a small hole at the top of a bar magnet. When the apparatus with one point only is charged with diluted acid, and brought into communication with the end of the magnet, placed vertically, the zinc cylinder revolves in a direction determined by the magnetic pole which is uppermost. With two points the copper revolves in one direction, the zinc in a contrary one. The magnet employed in the experiment requires to be powerful.

Ampere's Theory of Magnetism.—The general similarity of properties subsisting between a spiral conductor in the act of giving passage to electricity, and a magnet, led to a peculiar theory of magnetism, by M. Ampère. He assumes that the polarity of magnets is referable to the circulation within them of electric currents continually traversing the molecules of which they are composed, in planes parallel to their axes. Similarly he imagines the existence of electric currents in the earth; but more particularly on its surface, in the direction of east to west, in planes parallel to

the magnetic equator. A cause of the existence of such currents he supposes to be the heating influence of the sun's rays; for it should be mentioned, in anticipation of the subject of thermo-electricity, that heat is one great cause of electrical excitation.



Acting upon the suggestions of Ampère's theory,—that magnets are connecting bodies through which electricity passes in a spiral direction,—electricity has been applied to the formation of temporary magnets of enormous power. For the purpose of making these strong magnets, bars, either straight or bent in the form of a horse-shoe, of soft iron are used,—a material which assumes the magnetic influence much more readily than steel; but not, like the latter, giving rise to permanent magnets.

Fig. A represents an instrument of this kind. To avoid complexity of illustration, the wire (insulated) is represented as consisting of a single layer: the power of the instrument, however, is greatly increased by laying layer over layer on the insulated wire; the two series of wire-ends being collected each into one metallic combination, as represented in the diagram.

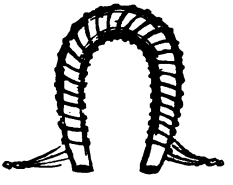


Fig. A.

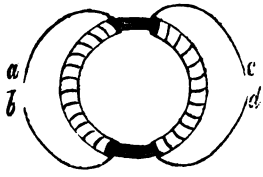
Magneto-Electric Phenomena.—After the direct relation subsisting between electricity and magnetism had been experimentally demonstrated, it occurred to various philosophers to imagine that an inverse order of mutual dependence might possibly be made apparent; that, as magnetism had been developed by electricity, so, conversely, electricity might be developed from magnetism. Now, a metallic wire, made to serve as a voltaic conductor, is, as we have already demonstrated, a magnet whilst the current is passing; therefore several of the phenomena comprehended under the head *magneto-electric* admit of two forms of expression, the meaning remaining unaltered. The resulting electricity may be said to be induced by the influence of another current of electricity, or it may be said to be induced by a magnet.

For the first development of *magneto-electricity* we are indebted to Mr. Faraday, who, reflecting on the effects of induction as caused by electricity at rest, was led to examine whether induction might not also result from electricity in motion. One of his first experiments, performed with the object of determining this question, was of the following kind*:—A copper wire 203 feet long was formed into a helix by winding it round a wooden roller; a second helix, equal in length to the first, was also formed on the same roller, in such a manner that the threads of each helix were mutually interposed. The wires of both, however, being insulated, there was no metallic contact between the two. The ends of one of these helices being placed in communication with a voltaic battery, and the ends of the other in connection with a galvanometer, a voltaic current was passed. Immediately the current began to flow, the magnetic needle of the galvanometer was deflected, and the deflection was repeated as soon as the contact was broken. Between the two periods in question, however, the galvanometer was not influenced. A repetition of this experiment demonstrated the fact that an electric current, transmitted from a voltaic battery through a wire helix, only induces a current in the

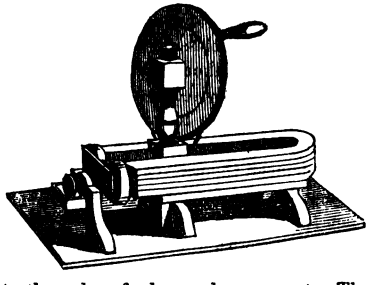
* "Phil. Trans.," 1831.

associated helix at the moments of making and breaking contact. In the former case, the direction of the induced current is opposed to the one which induces it; in the latter case, it is the same.

One of the next experiments performed in this line of illustration was the following:—A ring of soft iron was taken, and enveloped in two spiral copper wires, as represented in the diagram, each wire being insulated. Of these spirals, the ends of one (*a b*) were arranged for attachment with a voltaic combination; whilst the ends of the other spiral (*c d*) were placed conveniently for attachment with a galvanometer. A voltaic current being now caused to circulate through the spiral *a b*, the galvanometer-needle was immediately deflected. When both helices were in the same side of the ring, the amount of deflection was still greater.



A more convenient form of experiment consisted in winding the two helices on a cylinder of pasteboard, and connecting their ends respectively with a voltaic battery and a galvanometer, as before. On establishing a voltaic current, the galvanometer was again strongly deflected. On breaking the contact there was a similar result; the existence of the electric current being, in either case, rendered evident by interrupting the metallic circuit through the wire, when a spark was seen in the interrupted space. At the present time these magneto-electric machines are very common; the electric current being generated not by alternately making and breaking contact with a magnet, but by causing an armature or keeper, furnished with an insulated helix, to revolve very near to the poles of a horse-shoe magnet. The arrangement in question is delineated in the accompanying diagram.



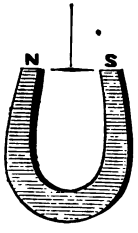
Dia-Magnetic Phenomena.—The tendency of iron to be attracted by a magnet long seemed to be an exclusive property to which no other body could lay claim: at length the metal nickel was admitted to participate in this quality, though to a lesser degree; and philosophers began to suspect that other bodies might be similarly endowed. To demonstrate the existence of this quality, however, was by no means easy, for the argument of the existence of iron as an impurity might be adduced, and, considering the great extent to which this metal is diffused, not without plausibility.

The merit of proving the metal nickel to be similarly endowed with iron as a magnetic agent is referable to M. Biot. That philosopher demonstrated not only the capability of this metal to be magnetically attracted, but the existence of a real magnetic polarity; and furthermore discovered the ratio of that polarity by comparison with an ordinary magnetic needle of steel. He found the directive force of the needle of nickel to be about one-third that of the needle of steel. These needles were each eight inches long, and two-tenths of an inch wide. Each weighed about five grains. In order to avoid all disturbance from the presence of iron, the nickel of which the needle was made had been carefully prepared by M. Thenard.

Thus the idea long entertained by philosophers, that iron was the only metal sus-

ceptible of magnetic influences, was rendered untenable. The experiments of M. Cavallo, which soon followed those of M. Biot, increased the list of *ordinarily* magnetic substances by adding to them brass (especially brass rendered hard by hammering); and also, under certain conditions, rhodium, iridium, and antimony.

The term *ordinarily magnetic*, employed above, requires a word of explanation. We shall see hereafter that although the property of being magnetically influenced is one common perhaps to all bodies, nevertheless the kind of influence differs. A suspended bar or needle of iron is attracted to either pole of a magnet indifferently; and, as a consequence of this property, if placed between the two polar ends of a horse-shoe magnet, such a bar will dispose of itself *axially*, to use the recognised term; that is to say, will place itself longitudinally between the two poles, as represented by the accompanying diagram.



Such is the normal condition of an iron or steel needle placed under the conditions described; and the result may be assumed as the type of ordinary magnetic influences. But if we should find hereafter—as will be the case—that certain bodies exist which if suspended similarly between the poles of a horse-shoe magnet, or in the magnetic field,—to use the language of philosophy,—are not indifferent to the polar influences of that field, but nevertheless do not place themselves in a similar position to a needle of iron or steel—then, although we must recognise the existence of a magnetic influence, some name must be devised to distinguish it from the phenomena of ordinary magnetism. Accordingly, where it was formerly the custom to divide bodies into magnetic and non-magnetic, they are now divided into magnetic and *dia*-magnetic: all bodies which demean themselves under magnetic influences like iron or steel being distinguished by the former, and all others by the latter appellation. Magnetic bodies, when freely suspended between the poles of a magnet, assume an axial condition of rest, —in other words, they place themselves lengthwise between the two poles. Dia-magnetic bodies, similarly suspended, assume the equatorial condition of rest—in other words, they place their length at right angles to the line joining the two magnetic poles.

Now that the universal susceptibility of ponderable bodies to magnetic influences is so incontrovertibly demonstrated, it may seem remarkable that the discovery was not made before; but the investigation was beset with many impediments. The earlier experimenters in this direction were embarrassed by doubts lest the materials employed might not contain iron; chemical science not being adequate to guarantee the total absence of that metal. Moreover, until the science of electro-magnetism had been established on a firm basis, and the power of readily creating energetic magnets made known, the number of experimenters having facilities for conducting the necessary investigations was comparatively small. Amongst the first who doubted the truth of the conventional division of bodies into magnetic and non-magnetic was Coulombe, who so early as 1802 began to investigate the results of suspending needles of various substances in the magnetic field. He arrived, however, at a false conclusion. Admitting the universal influence of magnetism on needles thus suspended, he fancied that influence to be of the same kind as is manifested on an ordinary iron needle. It is needless to indicate that his opinion, if borne out, would have been incompatible with the philosophy of dia-magnetism.

The experiments of Coulombe were followed up, and varied by the Abbé Hauy,

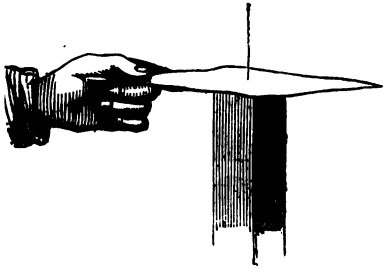
ithout, however, leading to any positive conclusions. Subsequently the same line f investigation was entered on by Becquerel, who made the important discovery that edles of white wood and of gum-lac, when suspended in the magnetic field, assumed e equatorial condition of rest. This may be considered, then, as the first beginning f the science of *dia-magnetism*. The investigation, however, of dia-magnetic relations as been followed up with the greatest ardour and success by Professor Faraday, to hom we are indebted for so many contributions to our knowledge of the forces hich actuate matter.

To expatiate further on the phenomena of magnetism and dia-magnetism would ad me too far from the domains of chemistry to be consistent with the object of this eatise. Suffice it to remark, that on submitting bars of various substances to the nfluence of the magnetic field, iron, nickel, and cobalt, all point axially; probably itanium, platinum, and palladium are in the same category; but all the other metals, ntimony, bismuth, copper, gold, &c., place themselves at right angles to the lines of agnetic force; they are repelled by either magnetic pole, and finally assume an quatorial condition of rest; in other words, they are dia-magnetic.

Underneath is a tabular view of bodies arranged according to their relations to agnetic force.

Magnetic Bodies.		Dia-Magnetic Bodies.			
Iron	Cerium	Bismuth	Cadmium	Silver	Uranium
Nickel	Titanium	Antimony	Sodium	Copper	Rhodium
Cobalt	Palladium	Zinc	Mercury	Gold	Iridium
Manganese	Platinum	Tin	Lead	Arsenic	Tungsten
Chromium	Osmium				

It may be as well, before finally dismissing the subject of magnetism, to remark, hat it is often a point of some importance in chemical investigations to determine hether a mineral be endowed with the power of magnetic attraction and repulsion. This is usually effected by bringing it near to one of the poles of a freely suspended magnetic needle to be examined. Far more delicate in its results, however, is the plan suggested by Professor Wheatstone, which is as follows:—Take a somewhat powerful bar magnet, fix it upright (it matters not which pole is uppermost); then lay flat upon it a thin disc of writing paper. Next take a delicate sewing-needle, break off its eye, and place it point downward vertically upon the disc of writing aper. Probably the needle may at first take a slanting direction, but a point may usually e discovered upon which the needle will stand upright. By gradually lifting the disc of aper upward it becomes evident that the magnetic force operating upon the needle, and nding to restrain it in the vertical position, will become less and less, until at length distance is attained, at which the needle is so delicately poised that it responds by eflection from side to side to the slightest magnetic influence.



Electricity as a Motive Force.—At periods very early in the history of ectrical science, the expectation was indulged that it might be susceptible of practical

application as a mechanical force; nor, considering the ultimate relation between the mysterious agent and the different forms of ponderable matter, did the opinion seem unreasonable. The very earliest electrical experiments—those involving frictional electricity—only manifest the phenomena of attraction and repulsion between material particles according to fixed laws, and at the operator's will. Now these conditions are what the mechanician would desire as the necessary elements in the generation of a mechanical force. Given the practical conditions of attraction and repulsion at the operator's will, the only remaining desiderata would be a sufficiency of force and a degree of economy compatible with the necessities of working expenses. Unfortunately, the force of electric attraction and repulsion is deficient in both these requisites. Its power is not only inconsiderable, but the expense of generating that power would be too great for practical economy.

The next idea relative to the employment of electricity as a mechanical force dates from the period when Cavendish, by the synthetical experiment of igniting oxygen and hydrogen, proved that water resulted from that combination. The suggestion was made of confining a mixture of oxygen and hydrogen, in the proportion of one volume of the former and two of the latter, in a cylinder, equivalent in function to the steam-engine cylinder, and igniting the mixture by agency of the electric spark. The treatment in question is immediately suggested by the instrument termed Cavendish's eudiometer; and one reason why the result could not answer the purpose intended will be made evident from a consideration of the structure of that instrument. Cavendish's eudiometer is made on the principle of withstanding the exercise of great internal force; for, in point of fact, although the combination of oxygen and hydrogen, in the proportions necessary to form water, finally results in contraction—tending towards the formation of a vacuum—nevertheless, there is a preliminary instant at which the force exercised is in the reverse direction—in other words, from within outwards. Hence any mechanical contrivance constructed with the object of utilising the ultimate collapse resulting from the union of oxygen and hydrogen, must be prepared for receiving the preliminary outward shock. Now, to accomplish this would be difficult, even supposing the economy of generating and uniting the gases required to be compatible with working conditions; which it is not.

Far more promising, at first sight, appears the employment of magneto-electric or electro-magnetic force; and, indeed, these forces have been applied to two good mechanical purposes at least—namely, to the construction of the electric telegraph and the electric clock. These, however, are quite exceptional cases; the mechanical force required for these purposes is only that necessary to generate a certain directive tendency, no further motive power being required.

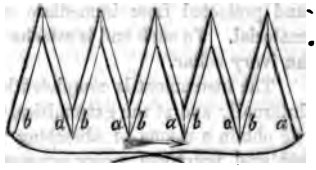
Understanding the term mechanical force in its ordinary signification—that is, anything equal in power to the force of steam—every attempt to generate it by means of electro-magnetic and magneto-electric combinations has failed. This result is contrary to what might have been expected. The attractive and repulsive force of magnets, artificially called into existence by means of voltaic combination, is enormous; the voltaic currents necessary for generating these magnets are but small; the expense of generating these currents insignificant; and the chemical products collaterally occurring during the voltaic action required, find a ready market. But one great difficulty besets the employment of these magnets, as mechanical agents; it is this:—the attractive and repulsive polarities diminish in some undetermined but rapid ratio, in proportion as the mass to be attracted or repelled is separated from the magnetic poles. This is a

difficulty inherent to the principle, and it seems incompatible with the successful employment of magneto-electric, or electro-magnetic force, to any practical extent.

Thermo-Electricity.—It has already been shown that heat is, under certain, if not under all, circumstances, a generator of electricity. For the most part, the electricity thus developed is lost to our appreciation; but by employing suitable apparatus the electricity developed by heat may be caused to flow in a definite channel, and to produce well-marked effects. The study of these effects constitutes the branch of science termed *thermo-electricity*. The electrical effects developed in this manner are not so powerful nor so brilliant as those resulting from voltaic frictional electricity; but they are exceedingly interesting, especially in relation to a means of estimating minute degrees of temperature. It is probable that the function of thermo-electricity belongs to all conductors of heat; but it is only under conditions of good conduction that the property becomes readily manifested,—in other words, thermo-electric combinations involve the employment of metals in their construction.

If a wire, equal in size throughout, and of any metal whatever, be formed into a ring, and heat applied to one part of the circumference, not the slightest tendency to an electric current will be manifested. But if the wire be unequal in size, or, what in practice amounts to the same, if a knot be tied in a wire of equal size throughout, then a current of electricity will be established, from the part to which heat is applied to the locality of the knot. Such, then, is the simplest construction of which a thermo-electric generator admits.

The thermo-electric disturbance and current are, however, most powerfully generated when two metals are used instead of one,—the conducting power of both the metals for heat being different. The most convenient form of combination results from the junction of the two dissimilar metals at an angle similarly to the letter V; and, perhaps, the best metals that can be employed in this case are bismuth and antimony. If heat be applied to the apex of junction, a current of electricity will become established in the direction from the point of junction towards the extremity of the metal which is the worse conductor for heat—that is to say, in the case under consideration, to the antimony.

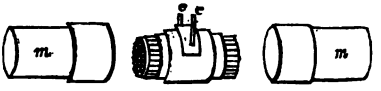


Experiments performed with the object of determining the relation in which certain metals stand to each other, in a thermo-electric sense, have led to the arrangement of the following series:—

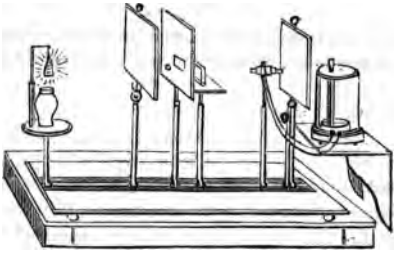
Bismuth	Tin	Zinc
Platinum	Copper	Iron
Lead	Silver	Antimony

From an examination of which we remark that the most powerful thermo-electric combination will result from the combination of bismuth with antimony. However, even by the combination of these extremes, the total amount of electricity generated is too inconsiderable to produce great effects; and to demonstrate the most interesting functions of thermo-electricity, compound arrangements of metallic pairs must be employed. The method of forming these compound metallic arrangements will readily suggest itself; nothing more being required than to join, by soldering, several of the V-shaped simple combinations together, as represented in the diagram above.

In this diagram the letters *a* and *b* stand for antimony and bismuth respectively, plates of which are seen to be joined alternately at their ends, so that every alternate soldering is in the same plane. The extremities of the terminal planes are furnished each with a wire, for the purpose of transmitting the generated electricity in any direction. The apparatus is electrically excited by the application of heat to one series of apices, whilst the other series are kept as cool as possible. It will be evident, on consideration, that the V-shaped combination is not a necessary condition to the existence of the instrument; indeed, the above-mentioned form is somewhat inconvenient, but at the same time it is very explanatory of its functions; therefore the subject of thermo-electricity is most profitably studied by commencing with its description. The idea of these compound thermo-electric combinations originated with Nobili, and it has been taken advantage of by Melloni in the construction of his exceedingly delicate thermometer. The idea of constructing a thermo-electric battery—as one of these compound arrangements may be termed—may have been suggested by the construction of a compound voltaic arrangement, to which it presents a certain similarity. In the functions of the two, however, there is this remarkable difference—by increasing the number of pairs in a voltaic battery, the intensity of the resulting electricity is alone increased; whereas, in a compound thermo-electric combination, both quantity and intensity are proportional to the number of pairs employed in the series. The thermo-multiplier of Nobili consists of about fifty pairs of antimony and bismuth bars, joined together by the alternate ends, and protected from immediate contact elsewhere by means of some non-conducting material. To each end is attached a wire, which is represented by *c c*, passing through an ivory collar.



The instrument is completed by inclosing it in two metallic sheaths, *m m*, blackened internally and at the extremities, but polished and bright elsewhere. Thus finished, we obtain a means of absorbing radiant heat, and communicating it to one series of soldered junctures, a consequence of which is the development of an electric current, which may be made to communicate its influence through the terminal wires, *c c*. These wires being placed in communication with a galvanometer, the magnetic needle of the latter is deflected proportionately with the amount of electricity set in motion, and therefore proportionately with the quantity of heat absorbed. By means of this delicate instrument, changes of temperature amounting to no more than the $\frac{1}{5000}$th part of a degree of Fahrenheit's scale are easily recognisable. The accompanying illustration represents the apparatus of Melloni, being a combination of Nobili's arrangement with the galvanometer, as employed for the purpose of ascertaining the transmissibility of heat (diathermaniety) of various laminæ.



Although I have mentioned the common galvanometer to be employed in connection with the thermo-electric bundle, yet, strictly speaking, this is not so. The wires are larger

than those of the ordinary galvanometer, and the length of wire or circuit is not so long as in the ordinary form of that instrument. This modification is rendered necessary by the very weak tension or power of overcoming obstacles possessed by thermo-electricity. The difference between *tension* and quantity as applied to electricity I have already explained at page 210 of this treatise.

An interesting correlation between heat and electricity is manifested by passing an electric current through a thermo-electric combination, whether simple or compounded. Under these circumstances, assuming the apparatus to have been of one temperature throughout at the commencement of the operation, the surfaces of junction become hot, thus proving that the same instrument which liberates electricity on the application of heat will liberate heat on the application of electricity. If a source of cold be applied to the extremity of the apparatus at which the electricity would have escaped, supposing the application of heat to have been made at the soldered junctions, then the latter portions of the instrument become greatly reduced in temperature—so greatly indeed, that if a little hole be bored into the substance of the metal and filled with a drop of water, the latter becomes speedily frozen.

A consideration of the laws of thermo-electricity led to some most interesting conclusions. For example: it presented us with a probable explanation of the cause of terrestrial magnetic direction. That a freely suspended magnet should tend to place itself in a line from north to south was long a mystery so remote from the conceptions of philosophers, that no hope was entertained of arriving at its solution. At present we have a plausible explanation of the phenomenon. It has already been demonstrated that a suspended magnetic needle, free to move in any direction, places itself at right angles to a neighbouring electric current: hence, in order to explain the directive tendency of a magnet from north to south, it is only necessary to assume the existence of an electric current at right angles to it. Now the earth is warmed by the sun's rays in the direction of east to west, and a consequence of this heating must necessarily be the generation of an electric current in the same direction. A consideration of the relations subsisting between electric currents and magnetic force will show that our globe should be magnetic in a line at right-angles to the ecliptic. In point of fact, it is very nearly so; and, probably, would exactly coincide with that line, were there no secondary electric agencies in operation. This explanation is in accordance with Ampère's theory of magnetism; for the purpose of illustrating which Mr. Barlow has constructed an apparatus representing the supposed magnetic condition of our globe in miniature. His apparatus consists of a hollow sphere of wood, in which electrical currents are made to circulate, similarly to the presumed direction of those in our own globe. By placing an astatic needle on various parts of the surface of the apparatus in question, it was found that all the phenomena of terrestrial magnetism were closely imitated.

THE CHEMISTRY OF INORGANIC BODIES.

To one who is but slightly acquainted with physical and chemical philosophy the term "inorganic" will require no explanation. It will associate itself with a series of bodies and phenomena standing well apart from all others by virtue of characteristics rather appreciated than capable of definition. To aver that inorganic bodies are those which are not endowed with parts capable of sustaining the functions of life, and that organic bodies are the opposite, is to rush at once upon the great difficulty. The question, What is life? forthwith presents itself for response, and the terms of this response have never yet been agreed upon.

Notwithstanding this theoretical indistinctness of characteristics, by far the larger portion of the bodies termed inorganic suggest no difficulty whatever in respect of the binary classification. It is only when we arrive at the more abstruse examples of combination that a question exists. The elementary bodies, whether non-metallic or metallic, are necessarily removed beyond the limits of doubt. A similar remark applies to all their binary combinations. Entering upon the domain of ternary, quaternary, and still more complex unions, doubts begin to arise whether the result should be considered *inorganic* or *organic*;—doubts, however, which rather belong to metaphysics than to physics, inasmuch as they are dependent on the relationship which may be deemed proper to subsist between certain qualities and certain definitions.

It seems to be an immutable law of nature that the boundaries which man sets up between different sciences, and different branches of the same science, shall be swept away by the progress of discovery. The time was when the expressions chemical and mechanical philosophy were considered to belong to two departments of science essentially different from each other; yet, since the molecular constitution of matter has been brought within the chemist's scope, that opinion has been necessarily abandoned. Again, in chemical science, acknowledged as such, the time was when bodies were divided, without doubt or question, into the three primary classes of Mineral, Animal, and Vegetable. As the tide of investigation rolled on, philosophers discovered that they were not in possession of any certain sign indicative of the limits between vegetable and animal life, when at once fell to the ground the triple classification of bodies, and the binary classification of inorganic and organic took its place. This latter, we have seen, is not free from doubts and objections; but we must retain it for want of a better.

Elementary Bodies.—Chemists are acquainted with 64 elementary or simple bodies; that is to say, bodies which have never yet been decomposed. The appended table represents their names, their conventional symbols, and their atomic weights:—

Aluminium . . .	Al. 13·7	Calcium	Ca. 20
Antimony	Sb. (Stibium) 12·9	Carbon	C. 6
Arsenic	As. 75	Cerium	Ce. 47
Barium	Ba. 68·5	Chlorine	Cl. 35
Bismuth	Bi. 213	Chrome	Cr. 26·7
Boron	B. 10·9	Cobalt	Co. 29·5
Bromine	Br. 80	Copper	Cu. 31·7
Cadmium	Cd. 56	Didymium	D.

Donarium	Do.	Pelopium	Pl.
Erbium	E.	Phosphorus	P. 32
Fluorine	F. 18·9	Platinum	Pt. 98·7
Glucinium	G.	Potassium	K. (Kalium) 39·2
Gold	Au. (Aurum) 197	Rhodium	R. 52·2
Hydrogen	H. 1	Ruthenium	Rt. 52·2
Ilmenium	Il.	Selenium	Se. 39·5
Iodine	I. 127·1	Silicon	Si. 21·3
Iridium	Ir. 99	Silver	Ag. 108·1
Iron	Fe. 28	Sodium	Na. (Natrium) 23
Lanthanium	La.	Strontium	Sr. 43·8
Lead	Pb. 103·7	Sulphur	S. 16
Lithium	L. 6·5	Tantalium	Ta. 184
Magnesium	Mg. 12·2	Tellurium	Te. 64·2
Manganese	Mn. 27·6	Terbium	Tr.
Mercury	Hg. 100	Thorium	Th. 59·6
Molybdenum	Mo. 46	Tin	Sn. (Stannum) 59
Nickel	Ni. 29·6	Titanium	Ti. 25
Niobium	Nb.	Tungsten, or Scheelium	W. (Wolfram) 95
Nitrogen	N. 14	Uranium	U. 60
Norium	Nr.	Vanadium	Va. 68·6
Osmium	Os. 99·6	Yttrium	Y. 32·2
Oxygen	O. 8	Zinc	Zn. 32·6
Palladium	Pd. 53·3	Zirconium	Zr. 22·4

Classification of the Simple or Elementary Bodies.—Various schemes of classification have been proposed or adopted by different authors for the classification of the simple bodies. Davy, Ampère, and Berzelius adopted the classification of electro-positive and electro-negative, modified by Faraday, for reasons already explained, into the classification of *anions* and *cathions*. Other chemists have divided elementary bodies into combustibles and supporters of combustion. Professor Graham separates them into groups dependent on a general analogy of properties, and more especially on their isomorphous replacement of one another. To the electro-chemical divisions the objection may be urged that they are either founded upon hypotheses, or that they are practically incomplete. The classification of combustibles and supporters is open to the graver objection, that in the act of combustion neither of the bodies mutually operating on the other can, in the strict acceptation of philosophy, be said to be exclusively supporter or exclusively combustible. As concerns the principles of classification chosen by Professor Graham, it seems open to no objection on the ground of philosophic appositeness, but, practically considered, it is not the most convenient.

The division which I shall pursue in this treatise is the one into which chemical elements naturally resolve themselves in the mind of the practical chemist, and this irrespective of any theoretical considerations. The classification in question is shown by the accompanying scheme—

- Simple bodies
  - Non-metallic
  - Metallic
    - Kaligenous
    - Terrigenous
    - Calcigenous

LIST OF NON-METALLIC SIMPLE BODIES.

Oxygen.	Bromine.	Sulphur.	Carbon.
Fluorine.	Iodine.	Phosphorus.	Hydrogen.
Chlorine.	Selenium.	Boron.	Nitrogen.

OXYGEN.

EQUIVALENT OR ATOMIC WEIGHT, 8.

SPECIFIC GRAVITY, 1·1057.*

WEIGHT OF 100 CUBIC INCHES, AT 30 IN. BAR. 60° F., 34·29 GRAINS.

If the importance of any element be presumed to bear a relation to the quantity of it existing in nature, oxygen is pre-eminent in this claim. From one-half to two-thirds of the surface of our globe and its inhabitants consist of oxygen. A consideration of the following facts will demonstrate the extent to which the preceding statement may be accepted as correct:—

It exists both in the organic and inorganic kingdom. It constitutes eight-ninths of water, and water covers about three-fourths of the surface of the earth. Of the dry atmosphere, oxygen constitutes twenty-three parts of every hundred, and eight-ninths of atmospheric vapour. Of the earth's solid crust at least one-third is oxygen, as will be rendered evident if we reflect upon the minerals of which this crust is chiefly formed —namely, for the most part of silica, carbonate of lime, and alumina. Silica alone constitutes 45 per cent. of the earth's solid crust. Silica, carbonate of lime, and alumina, contain respectively about half their weight of oxygen.

Some idea of the proportion in which oxygen exists in nature may be derived from the following tabular view:—

AMOUNT OF OXYGEN IN THE WORLD.

Animal	Principles	$\frac{1}{4}$	$\frac{3}{4}$	Oxygen is $\frac{1}{2}$ or $\frac{2}{3}$ of the globe.
	Phosphate of lime	$\frac{3}{7}$		
	Water	$\frac{8}{9}$		
Vegetable	Principles	$\frac{1}{3}$	$\frac{4}{5}$	
	Water	$\frac{8}{9}$		
Mineral	Silica	$\frac{1}{2}$	$\frac{1}{2}$	
	Alumina	$\frac{1}{3}$		
	Lime	$\frac{2}{5}$		
Ocean and waters		$\frac{8}{9}$		
Atmosphere		$\frac{1}{5}$		

The total quantity of oxygen required daily for the whole human population has been calculated at 1,000,000,000 lbs.; twice that amount for animals; and a quantity equal to the first to support the operations of combustion and fermentation;—thus giving 4,000,000,000 lbs. per diem. But the functions unenumerated requiring oxygen demand at least an equal amount to the sum total above given; therefore the total amount of oxygen required daily is no less than the enormous quantity of 8,000,000,000 lbs.

Without oxygen no ordinary form of combustion could take place; nor could animal and vegetable life be sustained. Without oxygen there would be no water—no atmospheric air. The most ordinary constituents of the soil would be wanting. There

* Dumas, "Ann. Chim. et Phys." 3me serie, iii., p. 275.

would be no clay, no flint, no potash, soda, lime, or magnesia. It is difficult for a chemist to picture to himself the sort of mass in space our world would be if deprived of oxygen. There could be no animal, no vegetable, no water; the most striking peculiarity of the landscape would be the never-ceasing presence of resplendent metallic masses.

As our world is now constituted there are very few metals discoverable in a native or pure state; they usually occur in combination and, for the most part, with oxygen. Gold and platinum are almost the only metals which invariably occur under the metallic form; but if oxygen were removed from the globe, then a long array of metallic bodies would shine out in full radiance: but the world would be a small one (considerably less than half its present weight), and a very dead and cheerless world—deprived of every trace of animal and vegetable life.

Historical Notice and Synonymes of Oxygen.—Before the time of Scheele and Priestley the atmospheric air was assumed to be a simple body—an opinion which was proved to be incorrect by the philosophers in question. To Priestley the honour is due of having first effected the separation of oxygen gas (1774). Subsequently, in 1775, the discovery was repeated by Scheele. The appellation of *oxygen*—in French, *oxygène*—was applied to it by Lavoisier, who also denominated it the *acidifying principle;* in German, it is termed *sauerstoff*. By Condorcet it was denominated *vital air*, seeing that the function of respiration depends upon its presence. Scheele called it *fire-air*—in German, *feuerloft*—from the circumstance that its presence is necessary to every ordinary case of combustion. The expression *dephlogisticated air* was applied to it by its discoverer, Priestley, and had reference to a belief that oxygen was deprived of a certain imaginary material known as phlogiston.

The word oxygen is a compound of the two Greek words *οξυς*, *acid*, and *γενναω*, *I generate*, thereby indicating that it is an acid former. The expression derives its origin, as we have already seen, from Lavoisier, a chemist who lived in the early part of the great French Revolution, and to whom the greater portion of modern chemical nomenclature is referable. The term oxygen was given to the simple body in question, in accordance with the idea of its being the universal acidifying principle. The expression is suggestive of the boldness of thought in which all subjects at that period of turmoil were approached. It intimates not only that oxygen was the acidifying principle of all acids known at the time of Lavoisier, but that it must necessarily be the acidifying principle of all acids hereafter to be discovered. This assumption was rather too bold; nor was it quite accordant with true logical inference to assume, that of two or more bodies entering into the composition of an acid, one alone should be regarded as the acidifying principle.

Nevertheless, the idea that oxygen was the universal acidifier took firm hold of the chemist; nor has the progress of modern discovery been able to supersede much of the nomenclature begotten under this supposition.

Forms under which Oxygen exists.—This element has hitherto been only obtained, uncombined, in the form of a gas; whereas many bodies, the familiar form of which is gaseous, may be obtained as liquids or as solids. Oxygen gas, however, is subject to a remarkable modification, or allotropic condition, to which the designation *ozone* has been applied. Under this head it will be described further on.

Preparation of Oxygen.—Although oxygen gas was originally discovered by distilling it from the red oxide of mercury, yet this is by no means the most convenient method of preparing it. The processes usually adopted are as follow:—

1. By applying furnace heat to black oxide of manganese in an iron bottle or retort.

The construction and arrangement of the iron retort in question have been already detailed at page 178; it only remains, therefore, to indicate the decomposition which ensues. Black oxide of manganese, regarded as to its composition, is the binoxide, sometimes called peroxide, of that metal, and is composed of one equivalent or atom of manganese + two equivalents or atoms of oxygen. Its symbolical expression, therefore, is Mn. O_2. In addition to the black, bin, or peroxide of manganese, there are two others—viz., the protoxide and the sesquioxide. The three may be represented as underneath:—

	Atoms.		Parts by Weight.	
	O.	Mn.	O.	Mn.
Protoxide of manganese	1	1	8	28
Sesquioxide of manganese	3	2	24	56
Binoxide of manganese	2	1	16	28

Now it will be evident that if heat be applied to binoxide of manganese, and sesquioxide of manganese remain, a portion of oxygen gas must have been evolved. This is what takes place in practice—every two equivalents of binoxide of manganese evolving one equivalent of oxygen. From a consideration of these circumstances we may regard the binoxide of manganese to be thus composed:—

Two equivalents or atoms of binoxide of manganese { 1 Equivalent or atom of oxygen. 1 Equivalent or atom of sesquioxide of manganese.

2. By distilling a mixture of black oxide of manganese and sulphuric acid in a flask or glass retort.

The decomposition which ensues is referable to the fact that sulphuric acid does not combine with binoxide of manganese, but readily combines with the protoxide of that metal. The result is, that from every equivalent of binoxide of manganese, one equivalent of oxygen is expelled; and each resulting equivalent of protoxide combines with an equivalent of sulphuric acid. The following diagram will serve to render the scheme of decomposition intelligible.

1 Binoxide of Manganese { 1 Oxygen ——— escapes.
1 Protoxide of manganese
1 Sulphuric acid ——— 1 Sulphate of protoxide (protosulphate) of manganese.

In conducting this operation, only enough sulphuric acid should be added to form a stiff paste with the powdered oxide. Care should also be taken that the flask or retort be uniformly wet by contact with the pasty mixture; otherwise fracture will probably ensue on the application of flame. This method of obtaining oxygen gas is now but seldom employed.

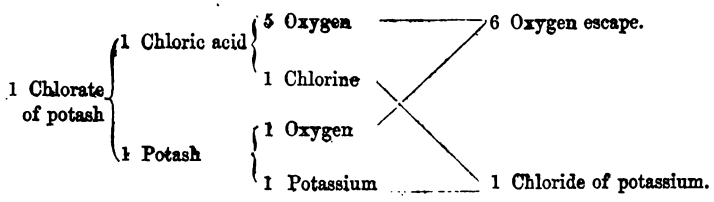
3. By applying heat to chlorate of potash in a small retort, or bent tube of hard German or green glass.

This is a very convenient plan of obtaining oxygen gas absolutely pure. The only disadvantage attending the operation is the high temperature necessarily required—a necessity which may be avoided by modifying the treatment as described in the next process. The decomposition which ensues is easily comprehensible. Chlorate of potash

is a compound of chloric acid and potash. Chloric acid contains five atoms of oxygen, and potash one. By the application of sufficient heat, all the oxygen (six atoms) is expelled, and chlorine, in direct union with potassium (chloride of potassium), remains. Symbolically, therefore, the decomposition admits of being represented as follows:—

$$KO, ClO_5 = KCl + O_6.$$

Or perhaps still more intelligibly by means of a diagram.



4. By distilling a mixture of equal parts of chlorate of potash and black oxide of manganese, or equal parts of chlorate of potash and black oxide of copper.

This is the process usually had recourse to for procuring small quantities of oxygen in the laboratory. The heat necessary to be applied is much less than in the previous instance, and the decomposition is more manageable. Notwithstanding the addition of oxide of copper, or oxide of manganese, both of which, as their name indicates, contain oxygen, the whole of the oxygen liberated comes from the chlorate of potash used. The presence of the advantitious oxide facilitates the decomposition of chlorate of potash by the operation of a force known as *catalysis*. Not that the term is to be recommended, seeing that it throws no light whatever on the nature of the change.

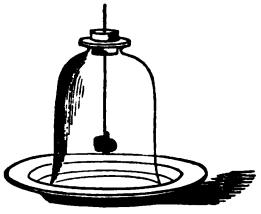
5. By exposing water to the decomposing agency of voltaic electricity, and collecting separately the oxygen and hydrogen gases.

At page 247, the method of performing this decomposition has been already explained.

Experiments with Oxygen.—The chief experiments which admit of being performed with oxygen gas have reference to the power of this elementary body as a supporter of combustion. Indeed, the very term combustion was formerly defined as being the rapid union of a body with oxygen. The impropriety of such a restriction has long been admitted, and the term combustion is now understood to express rapid chemical union attended with evolution of light and heat. Nevertheless, oxygen gas is the supporter of combustion, *par excellence*. By means of it all our ordinary fires are enabled to exist, and our chief sources of artificial illumination supplied.

Experiment 1. *Combustion of an ordinary Taper in Oxygen.*—Light an ordinary taper or candle; wait until the wick has become incandescent, then blow out the flame, and immerse the candle in a bottle of oxygen gas. The wick will immediately burst into flame, and continue to burn with exceeding brilliancy until all the gas has been expended. Instead of a candle, a small slip of wood, such as a match, may be employed. Thus the chemist has an excellent distinctive test of the presence of oxygen. Only one gas (the protoxide of nitrogen) can be confounded with it by the evidence of the test in question, even by the most inexperienced.

Experiment 2. *Combustion of Charcoal in Oxygen.*—Firmly attach a piece of charcoal to a copper wire, by twisting the latter round it; run the other extremity of the wire through a central hole in a small tin disc, and finally through a cork, as shown in the diagram. Light the charcoal by holding it in the fire or on a gas or blow-pipe flame, and immerse it in a jar containing oxygen, and standing in a soup-plate containing a little water. The charcoal will burn with far greater brilliancy than in the atmosphere, proving that oxygen gas is an excellent supporter of combustion.



Experiment 3. *Combustion of Phosphorus in Oxygen.*—Instead of the plain wire used in the preceding experiment, procure a small ladle of copper, as here depicted. It is commonly known as the deflagrating ladle, and may be obtained under that name in shops where chemical instruments are sold. Take a piece of phosphorus, not larger than a small pea; dry it by means of blotting-paper; place it in the deflagrating ladle; ignite it by contact with a hot wire; then plunge it into the jar of oxygen gas. The combustion of the phosphorus in this will be so exceedingly brilliant that the eye can barely tolerate the glare. The result of this combustion is a solid (phosphoric acid).

Experiment 4. Repeat the preceding experiment, substituting sulphur in place of oxygen. The combustion will not be so brilliant as the last; but, nevertheless, exceedingly beautiful.

Experiment 5. *Combustion of Iron or Steel Wire in Oxygen Gas.*—I have said iron or steel wire; but, perhaps, the most convenient thing to be used in this experiment is a length of steel watch-spring. Select a length proper for the experiment; pull it at either end, and pass it through the flame of a spirit-lamp or a bat's-wing gas burner, by which treatment the tendency to form a coil will be removed, and it will be rendered permanently straight. Attach one end to the cork and tin-plate disc, as in previous experiments, and wind round the other extremity a little cotton wool. If the latter be ignited, and the whole spring plunged into a jar of oxygen, the steel will take fire and burn most brilliantly, frequently throwing off globules of molten matter, which burn their way deep into the substance of the glass, and often, indeed, quite through.

Results of the preceding Combustions.—If the water contained in the soup plates employed for the experiments 1, 2, 3, and 4, be tested by means of blue litmus paper, the latter will be reddened, thus indicating the presence of acid matter. The combustion of iron yields no such acid result. This was an important subject of contemplation for Lavoisier, and it influenced the structure of his celebrated nomenclature. If the result of the combination of a body with oxygen was an acid, Lavoisier indicated the nature of the acid by employing the name (slightly modified) of the combining body; but if the result were not acid, he simply termed it an oxide. Thus, in a preceding instance, we obtain by the combustion of charcoal (carbon) in oxygen, carbon*ic* acid; but the combustion of oxygen yields oxide of iron. Now, in the instance of carbon, there is only one acid combination of it with oxygen; but had there been more than one, some means would be necessary for their verbal discrimination. Lavoisier determined, that supposing the acids of one series to be only two, the terminations *ous* and *ic* should respectively designate them; *ous* standing for the least rich in

oxygen, *ic* for the most rich. If more than two, the Greek prefix *hypo* he determined should be employed. A greater number of compounds than these terms would provide for was not known in his time. As an illustration of the working of this nomenclature I may cite the oxygen compounds of sulphur, which are all acid. For a long time only four of these were known, and their designation was as follows :—

	By Weight.		By Atoms.	
	S.	O.	S.	O.
Hyposulphurous acid	32	16	2	2
Sulphurous acid	16	16	1	2
Hyposulphuric acid	32	40	2	5
Sulphuric acid	16	24	1	3

Now it will be seen that hyposulphurous acid contains less oxygen than sulphurous, hyposulphuric less than sulphuric: thus, Lavoisier's provision suffices for the four; but eventually the number of sulphur and oxygen compounds became extended to seven, and chemists have designated them as follows :—

Sulphurous acid	$S\ O_2$
Sulphuric acid	$S\ O_3$
Hyposulphurous acid	$S_2\ O_2$
Hyposulphuric acid (*Dithionic acid*)	$S_2\ O_5$
Sulphuretted hyposulphuric acid (*Trithionic acid*)	$S_3\ O_5$
Bisulphuretted hyposulphuric acid (*Tetrathionic acid*)	$S_4\ O_2$
Trisulphuretted hyposulphuric acid (*Pentathionic acid*)	$S_5\ O_5$

The nomenclature, it must be confessed, is rather unwieldly, and far less expressive than a glance at the symbolical notation designating the acids in question. These chemical symbols are, in point of fact, checking the development of chemical nomenclature—the eye can more easily see a scheme of combination embodied in a symbol than the tongue can give it utterance.

Having thus far explained the scheme of the principles of chemical nomenclature devised by Lavoisier, so far as relates to the oxygen, it remains to examine the means by which he individualised several non-acid combinations of the same constituents. For this end the Latin prefixes *proto* and *per* were employed to denominate the smallest and the highest grade of oxygenation respectively, and the numerals *bi*, *tri*, &c. when more precise distinction was required. Occasionally, too, the Greek numerals *dis*, *tris*, *tetrakis*, were called into operation; also the Latin word *sesqui*. This general idea of the scheme of Lavoisier is all that I think desirable to give in this place. Familiarity with chemical nomenclature will best be acquired by explaining the meaning of other terms as they occur.

6. *Combustion of Potassium in Oxygen.*—This can be effected by heating potassium in a small copper ladle, and plunging it into a jar of oxygen gas. It is difficult, however, to make the potassium burn satisfactorily, in consequence of the crust with which it becomes enveloped. That crust, however, is potash—*an alkali*—and the result demonstrates how great was the impropriety of considering oxygen to be endowed with some necessary quality of an acidifying agent.

In all the preceding experiments, the law just enumerated would be found to hold good, provided the results of combustion were accurately collected and weighed. Practically, however, it is a difficult matter to collect the results of combustion, except

they happen to be solid. Now the result of burning iron in oxygen gas is a solid (oxide of iron), and the experimentalist may easily satisfy himself that the globules and masses of this substance produced weigh heavier than the original watch-spring employed. The exact amount of increase is equivalent to the weight of the oxygen absorbed; but this point is too abstruse for a learner to demonstrate.

The easily-recognised increment of weight acquired by the solid results of combustion in oxygen—such, for example, as the solid result of the combustion of the watch-spring—is intimately associated with the downfall of a theory already alluded to, termed the *phlogistic*. According to the theory in question, combustion was the concomitant, if not the result, of a loss of some imaginary principle termed *phlogiston;* but when it was discovered that the ashes or *oxide* of a metal actually weighed more than the original metal itself, the phlogistic theory would seem to have been abandoned as a necessity. Not so, however: its tenets had established themselves so firmly in the minds of chemists, that the argument of phlogiston, being a principle of levity, the antagonist of gravitation, was by some had recourse to. Nevertheless, the weakness of this argument is almost too palpable for comment.

Ozone.—Oxygen, I have remarked, can only be obtained uncombined in the state of gas; nevertheless, this gaseous form is susceptible of assuming a peculiar modification of qualities, by virtue of what is termed *allotropy* or *allotropism*. The explanation of this strange modification is totally unknown; but the result is a gaseous body, proved to be oxygen on analysis, yet differing from oxygen in many curious relations. Before, however, the student proceeds to study the nature of ozone, he had better make himself acquainted with a few properties of ordinary oxygen which have not yet come under his notice.

Ordinary oxygen is devoid of smell; it does not bleach; it does not corrode silver leaf; it does not tinge blue, a mixture of hydriodic acid and starch. Ozone has all these properties, and may thus be distinguished from ordinary oxygen.

Ozone was discovered by M. Schönbein of Basle. There are several methods of preparing it; but the following is most convenient:—Into a wide-mouthed bottle pour a little water, just sufficient to cover the bottom; scrape a piece of phosphorus to free it from external crust, and immerse it in such a manner that it shall be partially exposed to the air. Ozonation of the atmospheric oxygen speedily takes place, and the operation will be completed after the lapse of some hours. The ozonized oxygen should now be washed by transference from one jar to another several times, and the operation is complete. The gas thus prepared will be found to have acquired a peculiar smell, suggestive of the odour produced by a powerful electrical machine in good action. In point of fact, the electric spark, by its passage through atmospheric air, generates ozone; and the amount of ozone generally recognizable in the atmosphere is no doubt chiefly due to the operation of electric agencies.

HYDROGEN.

Equivalent or Atomic Weight, 1.
Weight of 100 Cubic Inches, 2·1492.
Specific Gravity, 0·0693.

When it is stated that hydrogen is a constituent of water, of all animals and vegetables, and of some minerals, enough will have been said by way of demonstrating

its importance in the scheme of creation. To the speculative philosopher, hydrogen presents other points of interest. Of all ponderable bodies it is the lightest; nevertheless, in many of its relations it demeans itself so much like a metal, that the chemist is almost inclined, bold though the idea may seem, to consider it and speak of it as such.

Several gases, as I have already indicated, admit of being reduced to the liquid and the solid conditions; but hydrogen has hitherto baffled every attempt of this kind. The fortunate chemist for whom the solidification of hydrogen is reserved may probably find it assume the aspect of a metal. Strange though such a result may seem, it is accordant with all the reasonings of chemists which have been brought to bear upon the subject.

Historical Notice, Synonymes, and Derivation of Hydrogen.—The term Hydrogen at present employed was first introduced by Lavoisier. It is derived from two Greek words—ὕδωρ, water, and γεννάω, I generate—signifying, therefore, the "water-former." The ancients regarded water as a simple substance, and the opinion held its ground until the time of Lavoisier. It is difficult to refer the discovery of hydrogen to any one philosopher, although the honour is usually referred to Cavendish, in 1766. The gas was developed in the course of many chemical operations, and had long been known under the appellation of inflammable air. In 1781, Watt and Cavendish proved the result of inflaming a mixture of oxygen and hydrogen gas to be water; and not long afterwards Lavoisier proved the truth of the English philosophers' synthetical experiment by the result of the analysis of water. The discovery of the relative volume of oxygen and hydrogen necessary to constitute water was reserved for Von Humboldt and Gay Lussac, being exactly one volume of oxygen plus two of hydrogen. Lavoisier and Meusnier had imagined the relation to be as 12 oxygen to 13 hydrogen; Fourcroy, Vauquelin, and Seguin, 100 to 205; and Nicholson and Carlisle, 72 to 143. Hydrogen is called by the French *Hydrogène*, by the Germans *Wasserstoff*. The term inflammable air was loosely applied not merely to hydrogen, but to other gases endowed with the property of combustion.

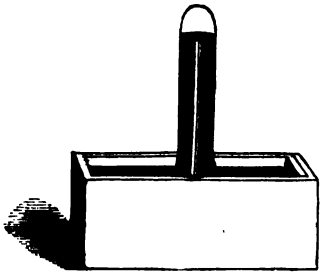
Sources and Preparation of Hydrogen.—Hydrogen never exists in nature uncombined. Its great storehouse is water; but it also exists in combination with phosphorus, sulphur, iodine, bromine, carbon, nitrogen, and almost all organic compounds.

Preparation.—Hydrogen may readily be evolved in the condition of gas, but under no other form. The source from which it is obtained is invariably water.

1.—*By bringing Water into Contact with Potassium or Sodium.*—Both these metals possess a remarkable affinity for oxygen; consequently, as soon as either of them is brought into contact with water, the latter is immediately decomposed, oxygen uniting with the metal, and generating an alkali, which remains in solution, the hydrogen escaping. If the experiment be conducted in the open air, the hydrogen takes fire; but if performed under a glass receiver, the hydrogen may be collected. The most efficient manner of conducting the experiment is as follows:—

Take a small glass cylinder closed at one extremity. Pour mercury into it until only about one inch remains unfilled. Into this remaining space pour water; then closing the open extremity of the tube, by means of the thumb, invert it over a surface of mercury in a common mercurial trough. By the preceding manipulation, it is evident that the small portion of water will find its way towards the closed end of the tube. The apparatus being thus disposed, a small lump of

potassium or sodium may be forced below the mouth of the receiving cylinder, and then allowed to escape. It will rise through the mercury, and come in contact with the water; by which contact the decomposition of the water will immediately ensue, its oxygen being appropriated by the potassium or sodium, and its hydrogen set at liberty in the tube. Although the plan described is theoretically the simplest which can be had recourse to, it presents some practical difficulties, in consequence of the extreme violence of decomposition which ensues. To modify this violence, it is advisable to substitute an amalgam of mercury and potassium, or sodium, in place of either of the alkaline metals alone.



2. *By Voltaic Agency.*—Under the head of voltaic electricity (p. 247), it has already been shown that water is susceptible of decomposition by the proper application of that agent. It is needless, therefore, to repeat the description in this place. A very convenient modification of the process, however, for obtaining hydrogen by means of voltaic agency—and which has the merit of not requiring a special voltaic battery—was devised by Fuchs, and is as follows:—Invert a platinum crucible in dilute hydrochloric acid, and whilst thus disposed, lay a flat zinc plate upon its base. By this disposition of parts voltaic energy results, and hydrogen gas collects in the crucible.

3. *By transmitting the Vapour of Water over small pieces of Iron contained in a Porcelain, or rather an Iron Tube, heated to redness in a furnace.*—Iron subjected to this operation is brought to the condition of black oxide, or the oxide which constitutes the scales of a blacksmith's forge, and which results when iron is burned in oxygen gas.

The experiment just described possesses much collateral importance, illustrating the fallacy of an opinion once prevalent, that the order of affinity between any two bodies might be determined by their order of decomposition. Supposing that, for the sake of argument, we recognise that assumption to be correct, then it would follow, from the preceding experiment, that iron must have a greater affinity for oxygen than hydrogen has for oxygen; but if a current of hydrogen be made to permeate oxide of iron, heated to redness in a tube, a decomposition precisely the reverse ensues: water is generated, and metallic iron set free. The fact is, that the order of affinity subsisting between any two bodies can rarely, perhaps never, be determined in this manner. This subject, however, has been fully treated of in a former part of this work (pp. 50, 51).

Perhaps the liberation of hydrogen from aqueous vapour, caused to pass over red-hot iron, is the readiest means of obtaining the gas in large quantities. It possesses an historical interest from the following circumstance:—

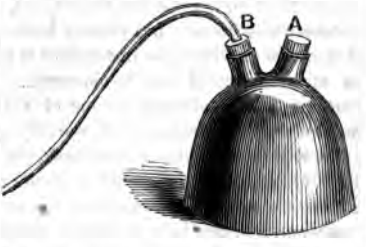
In the early part of the wars of the great (or first) French Revolution, the experiment was tried of employing air-balloons for the purpose of overlooking a hostile army, and noticing its disposition. Of course it became necessary to provide some portable and ready means of liberating hydrogen gas; and the process just described was adopted.

4. *From a mixture of Iron, or Zinc, Water, and Sulphuric Acid.*—If either iron or zinc, in small pieces, be brought into contact with water, slow decomposition of the latter results—oxygen is absorbed by the iron or zinc, and hydrogen set free. The process in question, however, is so exceedingly slow, that for all practical purposes it is useless. If, however, sulphuric acid be added to the water, decomposition ensues with great rapidity; and such is the process usually adopted. The most obvious explanation of the function performed by the acid is, that it dissolves the coating of metallic oxide so soon as formed; but it is scarcely satisfactory, at least in the case of zinc. Pure zinc is acted upon with extreme difficulty by dilute sulphuric acid; and pure iron is much less readily dissolved than the impure metal. Probably, therefore, the rapid solution of these metals in dilute sulphuric acid, under ordinary conditions of impurity, is referable to the existence of voltaic currents, which circulate from one portion of impure metal through the other.

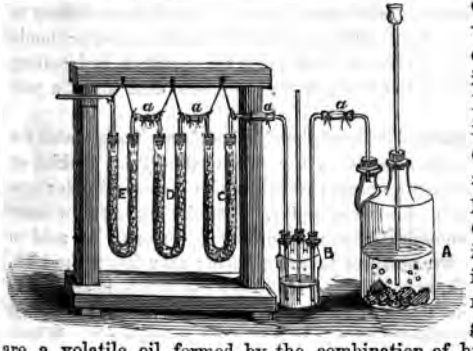
The chemical decomposition involved in the method of liberating hydrogen gas just described, is represented by the following diagram:—

1 Water { 1 Hydrogen _____ escapes.
1 Oxygen
1 Zinc _____ 1 Oxide of zinc
1 Sulphuric acid _____ 1 Sulphate of oxide of zinc.

For the purpose of generating hydrogen by the process just described, a glass retort or a glass flask, provided with perforated cork and bent tube, may be employed; but if large quantities of hydrogen gas have to be liberated, it is better to substitute for the glass retort or flask a copper vessel of the following description:—A B represent necks, each fitted with a good cork; the latter of which, or cork B, is perforated and adapted to a piece of pewter gas tubing, which serves to convey the liberated hydrogen into any convenient reservoir.



Properties of Hydrogen.—This element, as I have already remarked, can only be obtained in the state of gas, in which condition it is the lightest of all ponderable bodies, 100 cubic inches only weighing 2·1492 grs. Hydrogen gas, when quite pure, is almost devoid of odour; but, as ordinarily prepared, by means of zinc or iron and dilute sulphuric acid, or by the transmission of aqueous vapour over pieces of iron at a red-heat, it is obtained in combination with many impurities, and possesses a very disagreeable smell. These impurities are a volatile oil, formed by the combination of hydrogen and carbon; also certain gaseous combinations of arsenic or sulphur with hydrogen. From these adventitious



bodies hydrogen may be freed by bringing it into prolonged contact, first with aqueous solution of potash, which absorbs the offensive oil; next, with a solution of bi-chloride of mercury (corrosive sublimate), which, in its turn, absorbs the arsenical and sulphurous impurities.

A convenient arrangement for accomplishing the above-mentioned separation is represented on page 289. A is a generating bottle, into which dilute sulphuric acid and granulated zinc being thrown, hydrogen gas is developed. The disposition of the apparatus is such that the gas, as soon as developed, passes through the second, or three-necked bottle (B) which, containing a little water, separates all such portions of sulphuric acid which may happen to come over. Passing from this second bottle the gas is made to traverse a series of U tubes, conveniently suspended from a frame. The first of these tubes contains small fragments of pumice-stone, moistened with solution of potash; the remaining tubes contain solution of bichloride of mercury. Hydrogen gas thus treated may be considered free from admixture with any impurity except aqueous vapour, which, if desired, can be separated by transmission through a tube containing fragments of fused chloride of calcium, a substance which has powerful hygrometric properties, and is, therefore, commonly employed for the purpose of absorbing aqueous moisture.

It is scarcely necessary to remark, that a gas artificially dried, and intended to be kept dry, must not be collected over water in the ordinary pneumatic trough. A mercurial trough must be substituted. The description of a mercurial trough of elaborate construction has already been given at p. 182; but, for the greater number of purposes to which the instrument is applied, the expense of procuring so complete an apparatus need not be incurred. A very good mercurial trough, for general purposes, admits of being cut out of a solid block of wood, such as mahogany; and small mercurial troughs are frequently made of porcelain.

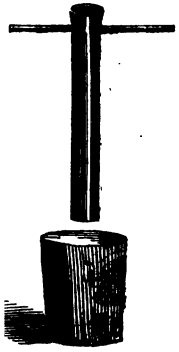
It will be evident that the trouble of drying a gas artificially, and collecting it over mercury, would be thrown away if the receiving-jars, or other vessels employed, were not dried also. The operation of drying a vessel is simple enough when the vessel possesses an orifice large enough to admit the hand, or when it has two apertures, so that a current of air can be established; but otherwise the operation is not so obvious as to render description unnecessary. Suppose, for example, it were desired to dry a Florence flask, moistened, we will assume, with pure water: it would be necessary to warm the flask by holding it near the fire; then inserting a tube, the operator should get rid of the major part of the vapour by blowing, but finish the operation by inspiring through the tube. A still better plan is to substitute for the mouth and lungs a pair of bellows.

Hydrogen Gas is Combustible.—Perhaps the simplest form of apparatus for demonstrating this, though not the most elegant, is the following:—Take a phial or small bottle, adapt to it an accurately-fitting cork, through which make a circular perforation, and fix in the latter the stem of a tobacco-pipe. Into the bottle throw some fragments of granulated zinc, and enough diluted sulphuric acid (one part of acid to about six or seven of water, both by measure) to cover them; then insert the cork, furnished with its tobacco-pipe shank, as described. Hydrogen gas will be immediately developed, and passing through the tobacco-pipe shank, will escape; but the first portions of gas which emerge will evidently be mixed with atmospheric air. When, in the operator's judgment, all the atmospheric air has been driven forth, and unmixed hydrogen is escaping, a lighted taper may be applied to the extremity of the tobacco-

pe shank, and the liberated gas will burn tranquilly, and with slight luminosity. If ie taper be applied *before* all—or, at any rate, the greater portion—of atmospheric air as escaped, an explosion will probably result—not dangerous, but sufficient to ow out the cork. Should an accident of this kind occur, it will least impress on the student's memory the valuable fact, that though hydrogen unmixed burns tranquilly, yet hydrogen mixed ith atmospheric air constitutes an explosive mixture—it constitutes, in point of fact, the fire-damp of coal-mines. A mixture of ve volumes of atmospheric air and two volumes of hydrogen gas the most explosive that can be formed of these two gaseous odies.

The apparatus just described is very rough—but I wish thus arly to impress on the pupil's mind the important fact that ough apparatus is valuable in its way. A very prevalent opinion xists that chemical science cannot be studied experimentally, ven in its rudiments and general principles, without the aid of xpensive apparatus; this is a mistake which cannot be too trenuously battled against. The first attempt of a young tudent of chemistry should be to make himself acquainted with principles; and ot unfrequently principles are better inculcated by rude and imperfect than by ighly-finished and perfect apparatus. The latter are frequently deficient in one mportant educational particular—they do not well make known the difficulties to be onquered in achieving a perfect result, and they prevent the learner from deriving the ducational benefit which mishaps and foiled attempts are able to confer.

The experiment just described involves the performance of an operation with which am to suppose the learner unacquainted, and which, therefore, should be illustrated. A cork has to be perforated with a hole, and this process, simple though it may appear, requires some little practice to do it well. Chemical apparatus makers sell instruments known as cork-borers. They are sold in sets, no two being of the same dimensions, and one fitting into the other. Each of these cork-borers is a brass tube, some four or five inches long, filed to a rough or saw-like edge at one extremity and left blunt at the other. Near to the blunt end each borer is pierced with a transverse hole, through which a piece of wire may be thrust, so as to enable the operator to give rotatory motion. When it is desired to perforate a cork, one of these borers is to be chosen, a little smaller than the tube intended to be finally thrust into the cork; then rotatory motion, accompanied by gentle pressure, being applied, a hole is speedily made. If the hole be too small, it admits of being enlarged by means of a rat's-tail file.



I shall now describe more perfect forms of apparatus for procuring a jet of hydrogen, or, indeed, any other gas, premising that the instructions o be given will not only refer to the particular gas under consideration, but to all gases whatever.

Fig. A represents an arrangement by the aid of which a jet of gas can be liberated from an ordinary bell-glass receiving jar. By reference to the illustrative diagram, it will be seen that the jar in question is supplied with a brass cap, into which is

screwed a stop-cock. Through the aperture of this stop-cock it is evident that gas must rush if the jar be forced down into the water of the trough by manual pressure. Should it be desired to obtain a smaller jet than that which would result from the mere stop-cock bore, such a jet may be readily made out of a glass tube, or even out of the shank of a tobacco-pipe. The chemist who works with gases must procure a few stop-cocks, with intermediate connecters; and when procuring them, he should see that they are cut with the same screw-thread. Much trouble, indeed, will be saved if the chemical student, in the getting up of his laboratory requisites, takes care to have but one screw-thread pervading all his apparatus in which a screw-thread occurs. By attending to this precaution, it is astonishing how much expense and trouble may be avoided.

Fig. A.

A lot of stop-cocks, with their accompanying connecters, is represented in the cut annexed. It may here be proper to remark, that in screwing together any combination of apparatus intended to be ultimately made air-tight, the tightness is not attempted to be given by any accuracy of the screw-thread itself, but by little collars of leather, card, or india-rubber, well oiled, and bearing against the shoulders of the apparatus *a b*. These little collars require a punch for their manufacture to cut the central holes, and neat operators will also employ a second punch to cut the external contour; but the latter part of the operation may be accomplished by means of a knife or a pair of scissors.

Another plan for obtaining a jet of gas (Fig. B) involves the use of a moistened bladder, or a bag of india-rubber material. It is scarcely necessary to mention, that the flaccid receiver in question must have securely tied into its mouth, by means of waxed thread, a brass connecting piece, which, being done, the method of filling it is easy by the process represented in the annexed cut. When filled, the bag is to be unscrewed from the bell jar, a jet attached, and the gas employed according to the nature of the desired experiment.

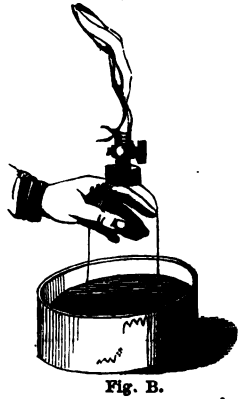


Fig. B.

By far the most eligible means, however, of obtaining a gaseous jet, if the operator possess a gas-holder, or gasometer, is by employing that useful instrument.

Fig. C represents a gas-holder of japanned tin-ware. To employ it the following operations must be gone through:—The cap *c* being firmly screwed on, and the stop-cocks S and S′ opened, water is poured into the reservoir R, when it is evident that the water, by descending through the stop-cock S to the closed reservoir G, will ultimately

fill it. The stop-cocks S and S′ are now to be shut, and the cap *c* unscrewed. The generated gas is now to be liberated through the aperture at *c* into the vessel, which it will ultimately fill, the charge of water running out. When quite full of gas—or, in other words, empty of water—the cap *c* is to be securely screwed on, and the apparatus is ready for application. Supposing that application to be the production of a jet, it is accomplished by pouring water into R, and opening both stop-cocks, when a current of gas will evidently escape through S′.

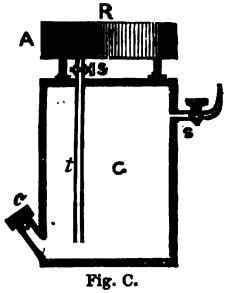


Fig. C.

Having, by either of the contrivances detailed, succeeded in procuring a jet of hydrogen gas, let the jet be ignited, and let the student observe how deficient it is in luminosity.

Chemical Result of the Combustion of Hydrogen in Oxygen.—If, over any conveniently-arranged jet of burning hydrogen gas, a dry bottle or receiving-jar be held, the interior of the jar or bottle will speedily be dewed by moisture—that moisture is deposited water, from which we arrive at the conclusion that water is a result of the combustion of hydrogen gas in atmospheric air. But atmospheric air is composed of oxygen gas, and another gas, not yet treated of—*Nitrogen*. Now, it is the oxygen part of the air which supports combustion; and hence it follows that water results from the combustion of hydrogen and oxygen gases.

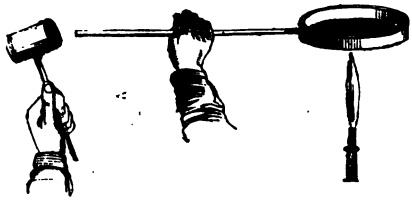
To demonstrate this proposition rigidly, it will be necessary to work with gases artificially dried, and, of course, to employ the mercurial pneumatic trough; a Cavendish's eudiometer, an air-pump, and electrical-machine will be also necessary.

The steps of the operation are as follow:—First screw the eudiometer firmly upon the plate of an air-pump, and exhaust the atmospheric air which it contains. Then turn the stop-cock, and attach the eudiometer to a receiving-jar, standing over mercury, and filled with a mixture of two parts by measure of hydrogen gas and one of oxygen. Now, throwing open the communication between the eudiometer and jar, it is evident that the former will become filled with the mixed gas; and here, assuming all the atmospheric air it originally contained to have been absolutely removed, this part of the operation might end. However, in practice, it is impossible to effect at once the extraction of all the atmospheric air; consequently the exhaustion process, by means of the air-pump, will have to be repeated, and the eudiometer connected with the mixed gas as before. When filled a second time the eudiometer must be removed from the jar, screwed upon its own foot, as represented in the diagram at page 231, and the contained gases fired by means of an electric spark. The eudiometer will be now dewed with moisture internally, and will contain nothing except this moisture, as admits of ready demonstration by opening its stop-cock under the surface of mercury, which, rushing up into the vacuum created, will fill the vessel. For this capital demonstration we are indebted to Cavendish.

Effects of Hydrogen Burning in Atmospheric Air.—On causing the ear to approach one of these burning jets, a series of explosions may be heard; but a far better means of rendering them evident is as follows:—Take a glass tube, open at both extremities, hold it vertically, and cause the hydrogen flame to burn a little way up the tube. By adjusting the tube, and allowing the jet to burn at different points of elevation, the point will most likely be discovered at which the glass-tube will be caused to emit a musical sound. If the first tube employed should not answer the

purpose, others may be tried. The musical sound in question results from vibrations generated by the series of little explosions. Instead of glass tubes, wine bottles—or, perhaps, still better, soda-water bottles—may be substituted.

A Burning Jet of Hydrogen Gas may be increased in Luminosity by the presence of Incandescent Solid Particles.—Construct a small sieve of wire gauze, and attach to it a stick, as represented in the diagram. Into this sieve place a little of the powdered substances presently to be described, and cause the substance to fall in showers upon the gas jet by striking the handle of the sieve with a small mallet.

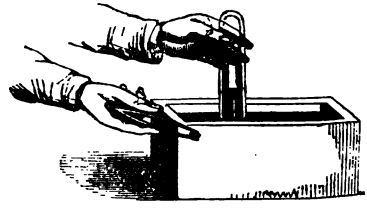


Charcoal Powder.—No sooner does the material touch the flame than the amount of light evolved from the latter is greatly increased; but the result is a mixed case, inasmuch as charcoal powder is itself combustible.

Lime, Magnesia, Alumina.—On substituting either of these bodies for the charcoal in the preceding experiment, an increase of luminosity also results, and the effect is in neither of these cases due to combustion. These experiments illustrate the conditions which require to be fulfilled in imparting luminosity to flame. The presence of incandescent solid particles is absolutely necessary to that result.

Influence of finely-divided Platinum upon a Jet of Hydrogen Gas.—By finely-divided platinum is meant not filings of that metal, or any mechanical preparation of the same, but one of two substances known respectively as spongy platinum, and platinum black; both of them will be fully described hereafter under the head of *platinum*. It suffices here to indicate the existence of these bodies, and their applicability to our present wants. Both spongy platinum and platinum black are endowed with the property of causing a jet of hydrogen to inflame when held in the latter. For convenience of manipulation it is usual to mix the comminuted metal with a certain amount of clay and sal-ammoniac, to moisten the whole with water, and to mould the pasty result into little balls, each about the dimensions of a pea. These clay platinum balls, after having been heated to redness, are ready for the purposes of experiment.

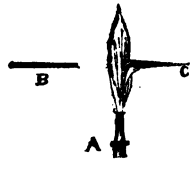
Experiment 1. Lay hold of one of these little balls, by the aid of a loop of platinum wire, and hold it in a jet of hydrogen gas. The pellet soon grows incandescent, even to whiteness, and the gas inflames. In like manner, these little pellets may be employed, instead of the electric spark, for causing the union of mixtures of oxygen and hydrogen, mixed or unmixed, with other gaseous bodies. Frequently, too, they admit of employment under circumstances when the electric spark would be inapplicable. For example, it has already been mentioned that the exact ratio of combination for oxygen and hydrogen gases to form water, is two measures of hydrogen to one of oxygen. This ratio may be varied to some extent in either direction—that is to say, either an excess of oxygen or of hydrogen, within given limits, may be employed, and



the electric spark is still effective, the overplus of either gas remaining uncombined; but if the correct ratio of admixture be considerably departed from, electricity can be no longer used as the combining agent, and the experimental chemist must have recourse to balls of spongy platinum. He does this in the following manner:—The mixture of gases being confined in a tube, or small jar, over mercury, one or more of the little balls, previously ignited in a spirit-lamp flame, is pushed, by means of a pair of forceps, underneath the orifice of the little receiving vessel, supported over a mercurial trough, and allowed to rise in contact with the gas. This being done, combination rapidly takes place.

Heat developed by Hydrogen.—*A Jet of Inflamed Hydrogen Gas, although slightly Luminous, develops much Heat.*—This proposition may be demonstrated by holding a piece of glass tubing in the ignited jet, and noticing the rapidity with which it fuses.

A Jet of Inflamed Hydrogen Gas has its Heating Powers greatly increased by passing through it a Jet of Oxygen.—This may be readily demonstrated by a contrivance of the following description. Let A represent a vertical jet of hydrogen gas, and B a horizontally arranged jet of oxygen. By combining the two the flame will be bent from its upward course to the direction C, at which point the most splendid effects of combustion may be produced. An iron nail held there speedily melts, so even does a tobacco-pipe or other piece of earthenware.



A certain Elevation of Temperature is necessary to the Existence of Flame.—This proposition is not only true as regards the flame of burning hydrogen, but of all flame whatever. Now, however, is a fitting opportunity for illustrating the general proposition.

Having bent a length of strong brass wire into the form of a ring at one extremity, lower the ring part on the flame of a small wax taper: the flame will be incapable of passing through the ring if the latter be sufficiently small; but a considerable amount of fuliginous matter will ascend through the ring, and may be re-ignited above it. By substituting a jet of inflamed hydrogen gas for the taper flame, a like result will supervene. In consequence, however, of the combustion of hydrogen giving rise to no fuliginous matter, one phase of the previous experiment will cease to be obvious. By diminishing the size of the ring, and using several of the latter, the wire employed may be of slighter diameter; and as the shape of the aperture is of no consequence, the material wire-gauze suggests itself as being the most convenient means of producing the desired result. If, then, a piece of wire-gauze be held over the flame of a taper, of a spirit lamp, of hydrogen, or indeed over any flame whatever, we shall find that the wire-gauze effectually prevents its transmission. This effect is referable to the cooling agency of the metal of which the ring, or net-like screen, is formed, and admits of several useful applications, as will be presently seen.

A Mixture of Oxygen and Hydrogen Gases in due Proportions is Explosive.—In an experiment detailed at page 231, when two parts by measure of hydrogen with one by measure of oxygen were confined in the eudiometer of Cavendish, and fired by means of an electric spark, perfect and instantaneous combination of the two resulted; but inasmuch as the mixed gas was securely confined, the union was

not attended by explosion. If, however, a similar mixture be now prepared, transferred to a strong soda-water bottle, and a flame brought near to the mouth of the latter, there will be a violent explosion; and here it may be useful to observe, that explosion is nothing more than the result of a series of waves developed suddenly in any gaseous medium. Whenever the phenomena of combustion are raised to their highest degree of energy, and the results of such combustion are gaseous or vaporous, explosion is the universal concomitant. Explosion is so usually associated with combustion, that we are apt to assume a necessary connection between the two: this supposition, however, would be incorrect. The only condition necessary to explosion is the occurrence instantaneously of violent aërial concussions. A well-known instrument termed the *bladder-glass* demonstrates the truth of this assertion.

The bladder-glass is an instrument something like an old-fashioned salt-cellar in shape, but open at each end. Over the larger orifice is securely tied, by means of waxed thread, a piece of moistened bladder, which latter, so soon as it is dry, constitutes a hard, tense drum-head in miniature. If a bladder-glass, thus duly prepared, be laid flat on the plate of an air-pump, its smaller orifice downward, and the pump set in motion, a vacuum will be created within, and the full force of atmospheric pressure will take place externally on the tense membrane. Usually this atmospheric force suffices to break the membrane with a loud crash.

A very elegant means of showing the explosive nature of mixed oxygen and hydrogen gases is by inclosing portions of it in soap-bubbles, and setting fire to the latter. The apparatus for accomplishing this result is exceedingly simple—a bladder, with stop-cock and tobacco-pipe attached, and a basin of soap-suds, being all the experimenter requires.

When a pyramidal assemblage of soap-bubbles have collected on the surface of the soap solution, and the bladder has been removed, the pyramid may be ignited by means of a taper. A very loud explosion results, but the experiment is free from all danger. Inasmuch as the mixed explosive gases are lighter than atmospheric air, bubbles blown with it may be detached, when they will rise towards the ceiling, and may be ignited in their upward flight.

The explosive qualities possessed by a mixture in due proportions of oxygen and hydrogen gases supplies us also with the rationale of the explosive nature of a mixture in certain proportions of oxygen gas and atmospheric air. Although a consideration of the nature and qualities of the atmosphere only admit of being fully discussed subsequently to the investigation of nitrogen, nevertheless the student having been already informed that the atmosphere is a mixture of oxygen and nitrogen, will comprehend, without difficulty, the significance of certain remarks about to be made. So long as hydrogen, either uncombined or in union with carbon, is burned as it escapes from a jet, no explosion can result; but if, instead of burning at once, it be mixed with atmospheric air, then explosion, on the application of flame, is imminent. Such dangerous mixtures frequently occur. Thus, for instance, a flaw, or aperture, may occur in an ordinary gas pipe, permitting the escape of gas into an apartment,

under which conditions explosion would probably result from bringing a lighted candle into the room; but a far more dangerous contingency follows the mixture of hydrogenous gas with atmospheric air in the narrow galleries of a coal mine. Acres of explosive gas may there be generated, waiting for the approach of a flame to ignite and work its desolation. A natural explosive mixture of this kind is known to miners as the fire-damp, and its effects are unfortunately too familiar for comment.

Now it is only possible for the coal-miner to carry on his operations by the aid of artificial light, and it is of the utmost importance to be possessed of a means of illumination that shall be incapable of exploding the artificial mixture. The first resource of this kind which suggested itself to the miner was the *steel-mill*, as it is ordinarily termed. It consists of a steel-cylinder made to revolve in contact with a piece of flint. The consequence of this motion is a shower of sparks; and as flame is absolutely necessary to the explosion of fire-damp, the steel-mill admits of being worked with impunity. Unfortunately, however, the illuminating power of this instrument is but small, and its use is otherwise inconvenient. Next followed the celebrated lamp of Davy, ordinarily known as the Davy lamp, the principles and construction of which will be rendered evident by a few words of explanation. A sheet of wire-gauze we have already seen to be an impediment to the transmission of flame. The idea occurred to Davy, that if a lamp-flame were to be altogether surrounded by a cage of wire gauze, such a lamp might be allowed to remain in an atmosphere of explosive gas with impunity. Davy's opinion is confirmed by practice, so long as the mixture of explosive gases remains perfectly tranquil; but the circumstance cannot be too strongly insisted on, that under these conditions alone of perfect tranquillity is it safe. It is also somewhat unfortunate for the posthumous fame of Davy, that he knew the lamp to be unsafe; indeed, in one of his descriptions of the lamp, he intimates, that if the miner should come near a current of gas, he should protect the lamp by his hat. Notwithstanding the frequent accidents which have occurred concomitantly with the use of Davy's lamp, a notion far more general than it is just still prevails, that the instrument is safe under all circumstances.

Unquestionably the lamp admits of being made safe by application of the principle so beautifully worked out by Davy—viz., that flame of any power may be extinguished by the intervention of tubes or orifices possessing a competent amount of cooling surface; but the melancholy experience of nearly forty years has amply demonstrated the small amount of reliance that should be placed on a single layer of wire-gauze. As regards the facility with which flame may be made to pass through the wire-gauze cylindrical screen, the records of numerous coroner's inquests bear striking though melancholy testimony. Miners have discovered the fatal secret of sucking out the flame by means of a tobacco-pipe, for the purpose of indulging in the luxury of smoking!

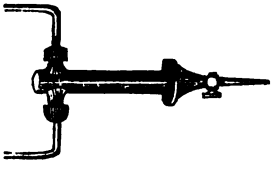
The Oxyhydrogen Light.—We have already seen that a very powerful flame results from the passage of a jet of oxygen gas through an ignited jet of hydrogen; still more powerful is the flame if the two gases, in due proportions, are mingled together. Various plans have been devised and carried into execution for effecting this without danger. Some of these I shall now proceed to enumerate.

Gurney's Hydro-Oxygen Blowpipe.—Taking advantage of the fact which we have already mentioned, that flame is retarded by the intervention of a sheet of wire-gauze, Mr. Goldsworthy Gurney imagined that several layers of wire-gauze might even be efficient in checking the progress of flames resulting from the com-

bustion of oxygen and hydrogen gases. The result justified his expectations, and Gurney's hydro-oxygen blowpipe is made in conformity with the principle in question.

The safety part of Mr. Gurney's instrument consists of a brass cylinder, into which as many layers as it will hold of accurately-fitting wire-gauze discs are tightly impacted. The reservoir part of the instrument admits of much variation. It may consist of an ox-bladder, or a gasometer, or an India-rubber bag. Mr. Gurney preferred the former.

Heming's Safety Apparatus.—Rather more simple, and it may be more free from danger, is the safety apparatus of Mr. Hemming: it consists of a brass cylindrical box filled with pieces of brass wire, each of the same length as itself, and tightly impacted together by means of a metallic spindle, driven by hammering through its central axis. The result of this arrangement will evidently be a series of tubular orifices, determined by the interstices between the associated wires. Far more usual, however, is it at present to rely on safety against explosion by retaining the gases each in its own reservoir, and mixing them in one common channel a little posterior to the jet. The accompanying diagram illustrates this form of construction.

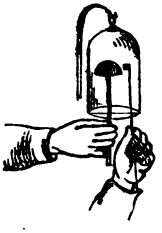


The oxyhydrogen flame is but slightly luminous in itself; but when caused to play upon certain solid bodies, more especially lime, the light evolved is stronger than almost any with which chemists are acquainted. Cylinders of lime are usually employed for this purpose; and the combination evolves what is usually known as the *Drummond Light.*

Relation of Hydrogen Gas to Sound.—All bodies, whether solid, liquid, or gaseous, are capable of transmitting sound; but the pitch of the sound, or its musical tone, will depend upon the density of the material through which it is transmitted. All our common ideas of sound have reference to atmospheric air as the conducting medium; it is instructive, therefore, to ascertain the properties of a gas so light and rare as hydrogen, when made to assume the functions of atmospheric air in this respect.

Alteration of the Human Voice by Hydrogen.—Hydrogen-gas is totally unable to support the functions of respiration; nevertheless, it may be breathed once or twice consecutively without damage to the constitution, or the production of any unpleasant symptoms. If a prolonged expiration be made, so as to expel as much as possible ordinary air from the lungs, and a full inspiration of hydrogen-gas be taken from a bag, bladder, or any other convenient form of receiver, the experimentalist will find, on speaking, that the character of his voice has totally changed. In conducting this experiment, absolutely pure hydrogen is unnecessary; but the zinc employed in the operation of making it should at any rate be moderately free from arsenic and sulphur. I have performed the experiment several times with hydrogen, prepared by means of the ordinary commercial zinc, and with no unpleasant effect. The experimentalist may vary the demonstration by endeavouring to play on any wind musical instrument, or by blowing a whistle.

A very elegant process for illustrating the acoustic properties of hydrogen-gas is by means of a bell. It is as follows:—



Suspend a receiving-glass, as represented in the diagram, and fill it with hydrogen by the process of displacement—that is to say, by liberating the gas underneath; then take a bell attached to a slender rod of metal, immerse the bell in the gas, and strike with a little hammer. The sound of the bell will be found to differ very much from the sound it naturally emits when caused to ring in atmospheric air.

Combinations of Hydrogen with Oxygen.—Hydrogen and oxygen unite in two proportions, forming respectively the *protoxide* (water) and the *peroxide* of hydrogen.

PROTOXIDE OF HYDROGEN (WATER).

	Grains.
Weight of 100 cubic inches at 62° Fah.	= 252·458.
Ditto ditto at 60° Fah.	= 252·5.
Atomic or equivalent weight	= 9.
Atomic or equivalent volume	= □

It has been already stated (p. 38) that water is a compound of oxygen and hydrogen gases, in the proportion of one volume of the former to two of the latter. Hence the combination admits of being symbolically indicated by the following scheme:—

O	H
	H

= Water.

Now, inasmuch as the atomic or equivalent volume of hydrogen is double the size of the atomic or equivalent volume of oxygen, it follows that water is a compound of one atom or equivalent of each of its constituents; for which reason it may be indicated by the symbolic representation of HO.

To direct the reader's attention to the immense importance of water in the economy of nature, would be a matter of pure supererogation. Suffice it to remark, that it is a constituent of every organised being, whether vegetable or animal—that it enters into the composition of numerous minerals. About nine-tenths of our own bodies are water; and in certain forms of animal life—the Medusæ, for instance—it exists in a much larger proportion.

Although water is so widely distributed throughout the world, it is never found pure. Owing to the properties of this liquid as a solvent, it takes up by percolation through the soil numerous adventitious bodies. Even rain and snow-water are far from pure: not only do they contain adventitious substances derived from the solid materials with which they may have come in contact, but they hold in solution variable quantities of matters which might be little expected, such as nitric acid, ammonia, and, if recent experiments are to be trusted, iodine. Nor should it be forgotten that water, even when purified from every kind of solid matter, may hold impurities of another kind—gases or air. Certain gaseous bodies, such as ammonia and hydrochloric acid gas, are absorbed by water with such energy that the pneumatic

trough does not admit of being employed for collecting them; and there are perhaps no gases whatever that cannot be absorbed, to some extent, by water. Atmospheric air is in this category. The quantity of it capable of absorption by water is very small; nevertheless, a portion is thus absorbed: and the fact is most important to be remembered, for without the presence in question of atmospheric air the functions of aqueous respiration could not be performed by fishes and other marine animals.

Although water never exists naturally pure, the kinds of impurities are almost infinite, and their proportions various. Absolutely pure warer, though fatal to aquatic animals, because it is unable to support their respiratory functions, may be ingested by aerial breathers without appreciable bad results. It is unpalatable, however, and perhaps not very conducive to health. Impure water, therefore—using the term impurity in its accepted chemical sense—is best calculated to fulfill the intentions of nature. But the impurities must not exceed certain limits, or the water, ceasing to be merely dietetic, becomes medicinal. Supposing this excess of impurities to be of a mineral character, as is usually the case, the designation "mineral water" is applied.

Division of Mineral Waters.—Perhaps the most convenient division of mineral waters is that adopted by the late Dr. Pereira, in his "Elements of Materia Medica." He groups them into the four classes of *chalybeate*, *sulphureous*, *acidulous*, and *saline*.

Chalybeate waters are those in which iron predominates—for the most part in the state of oxide held in solution by carbonic acid, though occasionally the acid present is the sulphuric. Sulphureous or hepatic waters owe their peculiarity to the existence of hydrosulphuric acid (sulphuretted hydrogen), in a free state, or to the presence of various easily-decomposed sulphurets. This variety of mineral water may be known by the nauseous odour evolved—an odour similar to that liberated from rotten eggs; also by their striking a black colour with solutions of lead, silver, bismuth, and various other metals.

The acidulous mineral waters owe their distinctive peculiarities to the presence of carbonic acid, either alone, or in combination, with bases. A small quantity of carbonic acid gas usually exists in all natural waters—seldom more than three or four cubic inches to the hundred, whereas the richest specimens of mineral waters acidulated by carbonic acid have more than 200 cubic inches to 100 of water. According to Alibert, the waters of St. Nectaire hold no less than 400 cubic inches in 100. Mineral springs of the acidulous class are not unusual in Germany; but that of Ilkeston, near Nottingham, is the only one we have in England.

Saline mineral waters are very numerous and important; their composition, too, is subject to more variation than waters of either of the preceding classes. It would be out of place in a volume on Chemistry like the present to treat of the composition of mineral waters more fully, or describe their medicinal virtues.

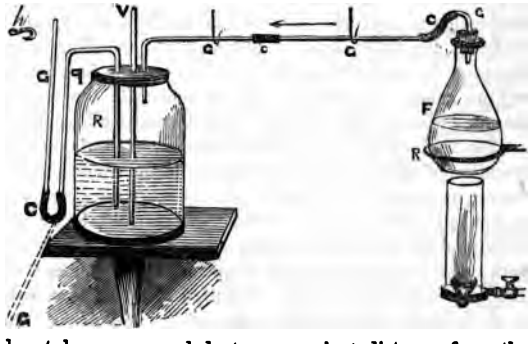
Without containing a sufficient amount of adventitious bodies to come under the denomination "*mineral*"—water naturally existing, and commonly employed, admits of a wide range of variation as to the foreign constituents which it contains. As a general rule, water drawn from a well or spring, is far more charged with saline impurities than water taken from a running stream; but, on the other hand, it is usually more free from organic impurities than the latter; hence, spring water is preferred as a drink. When employed, however, for the purpose of making vegetable infusions—such as tea or coffee, or for washing—any considerable amount of mineral bodies present in water, is most injurious, giving rise to the quality known as "*hardness*." None except those who have tried the experiment can imagine the efficacy of pure or

distilled water in extracting the virtues of tea and coffee, or the luxury of employing it for ablution.

Method of Testing the Purity of Water.—To determine the exact percentage of foreign materials present in any given sample of water, or their exact composition, involves a chemical analysis; but a very good practical notion of the relative amount may be derived from the evidence of a simple test—a solution of soap in alcohol.

To prepare this test-liquor, cut portions of soap in small pieces, agitate them with alcohol until dissolved, and secure the solution in a bottle. If a little of the solution be added to water distilled, or absolutely pure, no turbidity will result; nor will there be any perceptible turbidity, if, for distilled water, rain or snow water be substituted; but with the greater number of samples of spring water a visible turbidity will be apparent.

Pure or Distilled Water—The only methods of obtaining water in a state of absolute purity are its synthetical preparation, by causing oxygen and hydrogen gases to unite, and the distillation of ordinary water; the second method is alone of practical importance. Persons much engaged in the performance of chemical experiments require a copious allowance of distilled water, and usually procure it by the operation of a still and condensing worm, the construction of which I shall presently describe. Frequently, however, when the quantity of distilled water required is no more than a few gallons per week, as in laboratories of mere research, the necessity for a still may be altogether dispensed with, and the purity of the distilled water assured, by utilising the heat of Argand gas flames employed for the purpose of illumination. The apparatus required is of the simplest description; it may consist of a large glass flask, in which the water is evaporated, and a large bottle in which it is condensed, the necessary connexions being accomplished by means of glass tubing and india-rubber unions. I have an apparatus of the kind in my laboratory; it is constantly at work, and answers exceedingly well. The accompanying diagram is explanatory of its construction.



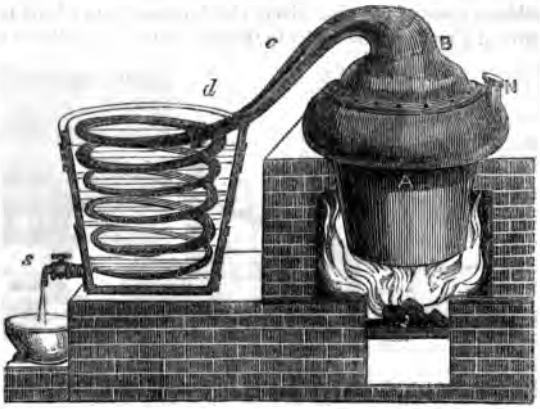
The large flask, F, holds about a gallon, and, as the diagram represents, is supported by a ring, R, attached to the wall. The gas flame is that of an ordinary Argand burner. C C C are connecting pieces, made by cutting off small lengths of vulcanized caoutchouc tubing, and joining the pieces of glass tubing, G G G G, together. The seemingly horizontal portions of the glass tube are suspended at a convenient distance from the ceiling by lengths of string, represented in the diagram, but not indicated by lettering; in reality, the portion in question proceeds with a slight fall in the direction of the arrows, for the obvious reason of determining a flow of condensed water in the required channel. Every portion of the glass tube is of the kind known as quilled glass, not much larger in diameter than the stem of a clay tobacco-pipe. The receiver is made

of a large druggist's show bottle, around the neck of which some folds of strong brown paper have been pasted, for the purpose of imparting roughness of surface, and giving firm hold to a sheet of india-rubber, which has been tied down over the mouth of the bottle like the parchment head of a drum. Through the india-rubber drum-head three small holes have been pierced in such manner as to enable the three glass tubes represented in the diagram to be passed through, air and steam-tight. The vertical glass tube, V, rising about six inches above the india-rubber drum-head, and passing almost to the bottom of the receiver, is for the purpose of equalizing the pressure of steam, by virtue of ordinary hydrostatic principles. It remains now to be explained that the quasi-horizontal portion of the tubular arrangement has been much shortened in the diagram for the sake of convenience. In my apparatus it is ten feet long, and might be extended still farther with some little advantage, inasmuch as the object desired is to cool the aqueous vapour by mere atmospheric influences, no artificial cooling agent being employed. As regards the method of getting water out of this closed receiver when required it is as follows:—A syphon of glass tube being joined by an india-rubber connecter to a vertical piece also of glass tube, the latter is retained *in situ* by means of the wire hook A, and so long as thus retained it is evident that no water will flow; but if the vertical piece be lowered in the direction of the dotted lines terminating at G', and suction be applied by the lips, a current of water will ensue. When the operator is desirous of causing the flow to cease he has only to lift up the delivery tube to its original position, securing it by the wire hook A. This hook, it must be remarked, is represented as totally separated from the apparatus, to avoid confusion in the delineation. A consideration of ordinary hydrostatic laws will demonstrate that one aspiration will serve for an indefinite period, and that water can be caused to flow at any period subsequent to the first operation by merely lowering the delivery tube to the direction of G. By the above-mentioned arrangement it follows that the distilled water contained in the receiving bottle being isolated from contact with the external air is always retained in a state of purity. Were it not for the protection of the caoutchouc drum-head, carbonic and sulphurous acids, resulting from the combustion of coal gas, also various mechanical impurities, would be absorbed, thus rendering the water impure. Whether the preceding or any other form of distillatory apparatus be employed, neither the first nor the last portions of steam resulting from any one charge of water should be collected: the former are liable to hold certain gaseous bodies in solution, the latter empyreumatic matters.

The Still.—The theory of distillation is exceedingly simple. It may be defined the operation of raising volatile substances in the condition of vapour, and condensing the vapour by application of cold. In its most restricted sense, the term "*distillation*" applies to liquids only; the term "*sublimation*" being given to the volatilization of solids, and the subsequent condensation of their vapour into the solid form once more. Both conditions, however, are frequently spoken of as "*distillation*;" and, indeed, the term is even extended to the evolution of gases from substances capable of yielding them, though no subsequent condensation takes place. On the large scale, the process of distillation is always conducted by means of a still and worm-tub, the former generating vapour, the latter condensing it. The construction of stills is very diversified, but the still in its simplest form is as follows:—

A is a vessel, usually of tinned copper, into which fluid intended to be distilled is poured through the aperture N, the latter being closed during the operation by a screw. B is the head or capital of the still, temporarily attached to the body by one of many

contrivances; such, for instance, as binding screws, a ground joint, or by the interposition of a paste or lute. C is the beak or spout of the still, terminating at the point *d*, by which it is connected to the worm or condensing part of the apparatus. This worm is a spiral tube of metal, immersed in a tub of cold water, and terminating at the stopcock *s*. The function of this worm is obvious: by contact with the cold water contained in the tub, its heat, and consequently the heat of the steam which pervades it, is rapidly absorbed, and thus condensation of the vapour is accomplished, which, assuming the liquid condition, finally runs off through the stopcock *s*.



It is evident that the perfection of the cooling instrument described above will be proportionate with the amount of cold that can be applied by means of the water in the tub; hence it follows that the more rapidly the water is changed, the better is the result. Moreover, inasmuch as hot water is specifically lighter than cold water, it follows that the contents of the worm-tub should be drawn off as near to its surface as possible, and should be replenished below.

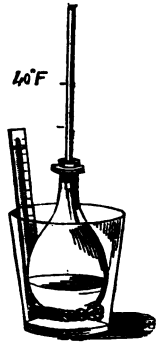
The form of distillatory apparatus known as the still and worm is very little employed in chemical laboratories of research, except for the purpose of distilling water; it almost exclusively belongs to the department of manufacturing chemistry. On the small scale the operation of distillation is usually conducted by means of flasks and retorts attached to some kind of condensatory apparatus. The various necessities involved in the course of distillatory operations require numerous kinds of apparatus for effecting condensation. For general purposes, however, the condenser known as *Liebig's* is unquestionably the best, and therefore merits a special description. It is constructed as follows:—

Procure a tube of brass, copper, or tinplate, of about two and a-half inches diameter, and not less than two feet long. Occlude either end of the metallic tube with an accurately-fitting bung, rendering the juncture between the cork and the metal water-tight by some appropriate lute. To this end there is nothing better than a stiff paste of white lead ground in oil, but, as it is rather long in drying, a lining of sealing-wax may be substituted for that end of the tube which will be furthest removed from the retort, flask, or other distillatory vessel, and which will therefore be the cooler of the two.

The next step in the manufacture of Liebig's apparatus consists in boring two lateral holes in the metal tube, one near either extremity. Into each of these holes solder a piece of gas-pipe about eight inches long; bend one of these pieces into the form of a syphon, and solder to the extremity of the other a small tin-plate funnel. It now only remains to perforate both corks, and to thrust securely through the perforations a length of glass tube, somewhat funnel shaped at one extremity, and the apparatus is complete. The functions of this elegant condenser will be readily understood by referring to the annexed diagram, which shows it mounted in connection with a distillatory retort and a receiving vessel.

Every theoretical condition for obtaining the maximum cooling effect of water is here applied by the most simple means. Inasmuch as the most elevated extremity of the metallic tube contains the hottest water, the final departure of that liquid should take place from the point in question. It *does* so, as the student will perceive, through the syphon-like termination; and a continuous stream of cold water is supplied at the lower extremity of the apparatus through the little tin-plate funnel.

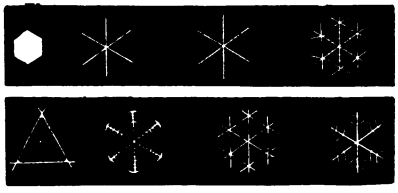
Temperature at which Water assumes its Maximum Density.—If water at some elevated temperature, say 210, be poured into a bulbed glass tube with long stem, and the apparatus gradually cooled down to the freezing point, 32° F., a peculiar phenomenon in relation to volume will be observed. In proportion as the cooling agency progresses the liquid column will be seen to descend, owing to the general contraction of the water operated upon. At length, however, at about 40° Fah., notwithstanding the continued agency of the cooling process, the descent of the column ceases, remaining for a moment stationary, and then once more rising, until the water has been cooled to 32° F. (the freezing point). This is a remarkable effect, and it is practically of great importance in the operations of nature. If water, like other bodies, acquired its maximum density at the point of solidification, ice would no sooner be generated than, sinking to the bottom of the generating water, it would there accumulate, and be removed so far from the influence of the sun's rays that it would never melt. The consequences of this result would be incompatible with the existence of aquatic life, and would, moreover, be highly injurious to terrestrial animals.



The expansive force of water, from its point of maximum condensation to freezing, is enormous. Its exact amount has never been ascertained; but the most violent mechanical effects have been produced by its agency.

Crystallized Water (*Ice*).—Water, in becoming solid by the agency of cold, usually

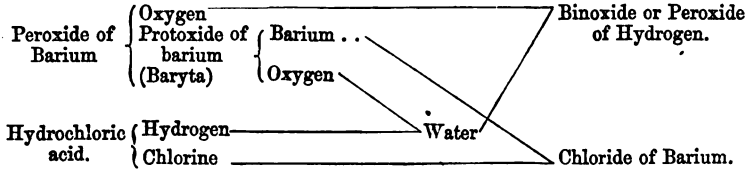
assumes the condition of an amorphous mass, in which the figures of no definite system of crystallization admit of being traced. Nevertheless, snow-flakes produced under certain atmospheric conditions—more especially those flakes which occur mixed with fluid water, and are usually denominated sleet—disclose regular crystallographic axes, belonging to the rhombohedral system. The subjoined diagram represents a few of these crystallographic forms. They are seen to be elementary regular six-sided prisms of six faces, grouped in stelliform arrangement around a centre, in such manner as to form angles of 60° and 120°. These, as crystallographers are well aware, characterize the rhombohedral system.



Binoxide or Peroxide of Hydrogen, HO_2.—Unlike water, which is one of the most common natural productions, the binoxide of hydrogen only admits of being prepared artificially in small quantities. It was discovered, in 1818, by M. Thenard, whose process of manufacturing it has never been improved upon.

The theory of its production is simple, although the operation, when practically carried out, involves many difficulties. We have already seen, when describing the production of oxygen, that the peroxide of manganese readily abandons a portion of its oxygen under suitable treatment. Many peroxides are endowed with a similar property; but if the peroxides of barium, or strontium, or potassium, be decomposed in contact with water, the liberated oxygen does not make its escape; it combines with water, and gives rise to the peroxide of hydrogen. The peroxide of barium was originally employed for this purpose by M. Thenard; and it is, in all respects, the most convenient.

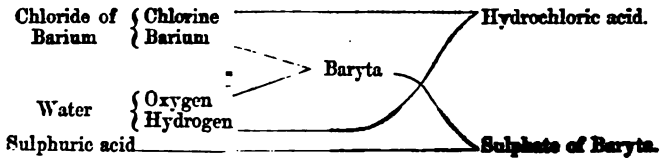
Process of Manufacture.—Saturate some peroxide of barium with water in a mortar until a somewhat liquid paste results. Add to the latter, by small portions at a time, a mixture of one part of ordinary hydrochloric acid and three parts water, stirring the mixture assiduously with a glass rod. The peroxide of barium is decomposed, and chloride of barium results, but no gas escapes. The appended diagrammatic scheme illustrates the nature of the change ensuing:—



Or, adopting chemical formulæ, the decomposition is expressed as follows:—

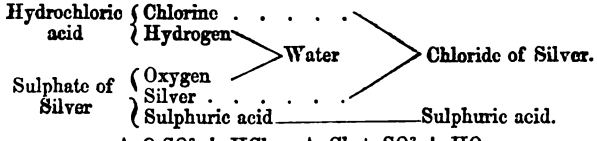
$$BaO^2 + HCl = BaCl + HO^2.$$

As soon as a sufficient amount of hydrochloric acid has been added to saturate the baryta, small successive portions of sulphuric acid are poured in, by which treatment sulphate of baryta is formed and precipitated, leaving the supernatant liquor a mixture of hydrochloric acid and peroxide of hydrogen, as represented by the following diagram and formulæ.



$$BaCl + HO + SO^3 = BaO.SO^3 + HCl.$$

Sulphuric acid is now cautiously added, care being taken not to supply it in excess. Sulphate of baryta is separated by filtration through cloth, and a liquor is at length obtained strongly impregnated with peroxide of hydrogen. This liquor is to be mixed with more peroxide of barium, and the operations already described repeated, until a fluid strong in peroxide of hydrogen remains. Sulphate of silver now being poured in, chloride of silver deposits, and sulphuric acid re-dissolves in the liquor.



$$AgO.SO^3 + HCl = AgCl + SO^3 + HO.$$

Finally the sulphuric acid is precipitated by a solution of baryta, added by successive small portions in such manner that no more than the exact amount required for decomposition may be poured in. The liquid is once more filtered, and evaporated under the receiver of an air-pump containing a dish of sulphuric acid. By these complicated operations the peroxide of hydrogen may be obtained quite pure, and in a high state of concentration.

One essential condition necessary to the success of the whole process has now to be indicated. The solution during the course of treatment must be immersed in ice, otherwise the decomposition of the peroxide of barium develops so much heat that the peroxide of hydrogen is not formed.

Properties.—The peroxide of barium reduced to its highest degree of concentration is a colourless liquid of syrupy consistence, endowed with a peculiar and characteristic odour. Its specific gravity is 1·453, and no degree of cold has hitherto sufficed for its congelation. It is liable to be decomposed by slight causes, especially when pure. The presence of a little acid renders it more stable.

Uses.—Peroxide of hydrogen has not hitherto been applied to any useful application; but if some easy process of manufacturing it could be devised, there is reason to believe it would be valuable in this respect. Its employment has been suggested for restoration of the whites of oil-paintings, which it accomplishes at once, converting the blackened carbonate of lead, or rather *sulphide* of that metal, into the white sulphate.

NITROGEN, OR AZOTE.

Equivalent, or atomic weight . . .	14
Specific gravity	0·9713
Weight of 100 cubic inches . . .	29·73 grains (Davy).

Derivation of Term.—The expression nitrogen (the nitre-former) was given to the element under consideration, because of its being a constituent of nitrate of potash (common nitre), which is the crystalline result of the union of nitric acid (aquafortis)

with potash. The term azote is derived from a combination of the Greek privative α, with the word ζωή *life*, thus indicating a leading characteristic of the element—its inability to support the function of respiration.

History.—Dr. Rutherford, of Edinburgh, was the first who appears to have discovered nitrogen gas as individualised from many other gaseous bodies to which the general term, mephitic air, had previously been applied. This occurred in the year 1772. Subsequently Lavoisier, by a beautifully-devised experiment, separated it from the atmosphere, of which he proved it to be a universal constituent. Scheele, without previous acquaintance with the experiment of Lavoisier, effected the same demonstration shortly afterwards, and thus secured to himself the merit of an original discoverer.

Synonymes.—In French the element under consideration is known as *nitrogène*, or *azote*; in German, *stickstoff*.

Form under which Nitrogen exists.—Nitrogen has hitherto been produced only under one form of material aggregation—namely, as a gas.

Preparation of Nitrogen Gas.—If a common taper, or piece of wood, charcoal, or indeed any other combustible body, be burned in atmospheric air, the results of combustion separated, and the remaining gas collected, it will be found unable to support combustion a second time. This is owing to the absorption of oxygen by the combustible. Theoretically, therefore, nitrogen should be procurable by burning away the percentage of oxygen existing in the atmosphere. Practically such is the kind of operation followed; but not every combustible will suffice. One is required that has a powerful affinity for oxygen; and which is, therefore, capable of removing every trace of that element. Phosphorus is the substance generally employed for that purpose.

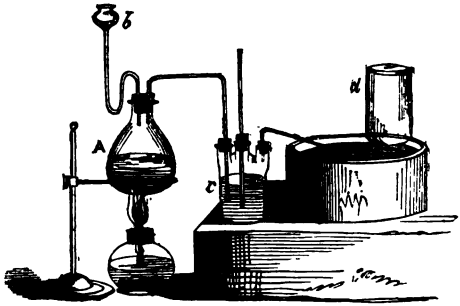
Process 1.—Over the shelf of a pneumatic trough, containing a proper amount of water, float a little dish of porcelain, or metal, containing a piece of phosphorus. Ignite the phosphorus by contact with a hot wire, then cover it with a glass bell-shaped deflagrating jar. Violent combustion will ensue, and the bell-jar will be speedily filled with vapours of phosphoric acid; the latter, however, is soluble in water, and, therefore, ultimately disappears if the jar be allowed to stand for a sufficient time over water. Its removal may be effected still more rapidly, however, by transferring the contents of the bell-jar to another vessel under water, and repeating the transference until absorption of the phosphoric acid has been complete, which may be known by the transparency of the inclosed gas, which is nitrogen almost pure. If required to be quite pure, and to be made by the operation just described, the small amount of carbonic acid always present in atmospheric air must be separated, by means of prolonged contact with fused potash, before the removal of atmospheric oxygen by means of phosphorus is proceeded with.

Process 2.—Red-hot copper speedily removes oxygen from atmospheric air, and, therefore, sets nitrogen free. Taking advantage of this fact, a ready means of producing nitrogen is suggested. The necessary disposition of apparatus will be as follows:—Fill a tube made of hard glass with copper turnings or shavings; heat the tube to redness in a furnace or over a few pieces of burning charcoal, and transmit through it a graduated stream of atmospheric air. Decomposition rapidly ensues: and if the copper turnings be sufficient in quantity, and the current of atmospheric air sufficiently slow, nitrogen, unmixed with any oxygen, will be evolved, though, of course, slightly contaminated with the small portions of carbonic acid invariably present in atmospheric air. If the air, before being subjected to the agency of red-hot copper, be made to permeate a tube containing caustic potash, all the carbonic acid will

be removed; and a second tube filled with pumice-stone, moistened with oil of vitriol, will also effect the separation of every trace of atmospheric moisture.

Process 3.—Nitrogen admits of being liberated in a condition of great purity by decomposing ammonia by chlorine. Ammonia is a compound of hydrogen and nitrogen, in the atomic proportions of three of the former to one of the latter. One part of the ammonia suffers decomposition in the preceding operation; chlorine, by uniting with hydrogen, forms hydrochloric acid, which latter, uniting with some ammonia still remaining undecomposed, generates hydrochlorate of ammonia, whilst nitrogen, thus isolated, makes its escape.

The apparatus necessary for accomplishing this decomposition is represented underneath. The glass flask A contains some finely-powdered peroxide of manganese, upon which a portion of hydrochloric acid is poured through the bent tubular apparatus *b*. Heat being applied, chlorine is evolved; and passing into the ammoniacal solution contained in the Woulfes bottle *c*, the play of decomposition just indicated takes place. Gaseous bubbles, perfectly devoid of colour, are evolved; and passing into the receiving-jar *d*, are there collected. The gas is nitrogen.



This process may be productive of great danger in negligent hands, owing to the formation of the chloride of nitrogen, the most violently-explosive substance, without exception, known to chemists. So long, however, as the Woulfes bottle contains a well-marked excess of ammoniacal solution no danger can arise from this source.

Properties.—Nitrogen gas is characterised by its strictly negative properties. It is neither acid nor alkaline. It is not combustible, nor does it support combustion. It does not yield a precipitate with any chemical agent. It has neither taste nor smell. The incapacity of nitrogen to support the respiratory function has already been adverted to; nevertheless, it cannot be actively injurious to animal life, seeing that it constitutes four-fifths of atmospheric air. Nitrogen gas is capable of solution in water to a very slight extent, a thousand volumes of water absorbing about twenty-five.

THE ATMOSPHERE.

Weight of 100 cubic inches	31 grains (Prout and Dalton).*
Specific gravity	1 (or unity).

Atmospheric air is regarded by chemists as a mixture—not a chemical combination—of oxygen and nitrogen gases, in the proportion by volume of one to four, or at least very nearly, together with variable amounts of aqueous and other vapours, and a small quantity of carbonic acid. In addition to the preceding, which may be termed normal atmospheric constituents, there are always present certain gaseous and vaporous results of animal and vegetable decompositions.

Lavoisier, as I have already stated, was the first who determined the atmospheric composition. His process of determination consisted in heating mercury confined in a

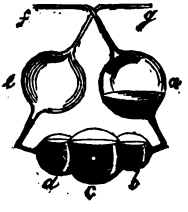
* See pages 166, 169.

limited volume of air for many days in succession; by which means the quicksilver, to use the expression of that day, was calcined (brought to the condition of red oxide of mercury). Lavoisier noticed that the volume of atmospheric air exposed to this operation became decreased in bulk, evidently from the absorption of something, and that the remaining gas no longer supported combustion or animal life. It was nitrogen.

He then collected the red oxide of mercury, exposed it to heat in a glass tube, by which treatment oxygen was evolved; and he demonstrated the leading qualities of oxygen now so familiar to chemists, and which, under the head of oxygen, have already been detailed. He finally mixed the remaining nitrogen and the evolved oxygen together, and reproduced a gaseous mixture, corresponding in every respect with atmospheric air—which indeed it was.

Determination of the Composition of Atmospheric Air.—The analysis of atmospheric air involves two kinds of processes; one for determining the amount of aqueous vapour and carbonic acid present, the other for indicating the percentage amount of oxygen and nitrogen gases. Carbonic acid is usually removed by means of caustic solution of potash, through which the air is caused to pass in small bubbles. Aqueous vapour may be removed by causing the air to permeate fragments of chloride of calcium in a tube, or fragments of pumice-stone thoroughly moistened with sulphuric acid.

The most convenient instrument for effecting the removal of carbonic acid from gaseous mixtures, wherewith it may coexist, was devised by Liebig, and is represented in the annexed cut. It consists of a glass tube bent into the form of a triangle, subsequently to the formation in its length of a series of bulbs. Solution of potash being introduced by aspiration into the three horizontal bulbs until they are almost filled, and partially into the others, the apparatus is ready for use. It will be evident that by establishing a connection between the extremity *g* and any other tube liberating gas, the latter will be caused to bubble through the potash solution under the restraint of some slight pressure, this being the condition most favourable to absorption of carbonic acid. It will also be evident, on consideration, that the amount, whether of atmospheric vapour or of carbonic acid, contained in a given volume of atmospheric air, may be readily determined by weighing the chloride of calcium tube and potash bulbs respectively.



Determination of the Relative Amount of Oxygen and Nitrogen present. 1. *By the combustion of Phosphorus.*—The process of liberating nitrogen by the combustion of phosphorus in atmospheric air effects the analysis of that air; but there are certain difficulties in practice which militate against a correct result. A more correct method of proceeding is the following.

2. *By the Prolonged Contact of Phosphorus.*—A simple arrangement for conducting this operation is the following:—Take a small tube retort, drop into it a piece of phosphorus, and insert the mouth of the retort in a glass of mercury. Dispositions having thus been made, gradual absorption of the oxygen will ensue, and the amount or volume of nitrogen remaining may be transferred to a graduated glass tube, and estimated with facility. A still more correct plan of obtaining a similar result consists in casting a small ball of phos-

phorus, with the end of a platinum wire in its substance, and elevating the ball into a tube containing atmospheric air over a surface of mercury, as represented in the preceding diagram. The operation of casting the ball of phosphorus must necessarily be performed under the surface of hot water.

3. *By a Solution of Sulphate of Iron saturated with Binoxide of Nitrogen.*—This solution rapidly absorbs the oxygen of atmospheric air, and liberates nitrogen, thus effecting the analysis; but the process is not frequently adopted in practice.

4. *By passing an Electric Spark through a mixture of Atmospheric Air and Hydrogen.*—This process involves the employment of the eudiometer, an instrument the various forms of which have already been explained at page 231. The theory of this process is very easy, nor is its execution difficult. The result of detonating a mixture of atmospheric air and hydrogen by the electric spark, is the formation of a portion of water, the original bulk of gaseous mixture being proportionately decreased. The decrease of gaseous bulk can be readily seen by inspection; and from a consideration of its amount the bulk of oxygen originally present in the mixture under treatment is at once determined, one-third of the diminution being equivalent to the original bulk of oxygen. The rationale of this will be evident when we consider that two volumes of hydrogen unite with one volume of oxygen to form water, and that to the production of water alone is the diminution referable.

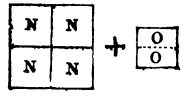
5. *By immersing a spongy Platinum Ball in a mixture of Atmospheric Air and Hydrogen.*—Directions for operating with spongy platinum, as a substitute for an electric spark, have been already given at page 294.

The results of innumerable analyses have proved that atmospheric air is a mixture of oxygen and nitrogen gases in the following proportions:—

COMPOSITION OF THE ATMOSPHERE.

By Measure.		By Weight.	
Oxygen . .	20·90	Oxygen . .	23·10
Nitrogen . .	79·10	Nitrogen . .	76·90
	100·00		100·00

It will be seen that the proportions given are very nearly in the ratio of four volumes of nitrogen to one of oxygen; or—



and, indeed, the opinion is entertained by many persons that any discrepancy from this exact ratio, as evidenced by analyses, is solely referable to errors of manipulation. Other chemists, on the contrary, believe that the variation is too considerable for explanation by that hypothesis, and found on this circumstance an argument in favour of the theory that atmospheric air is not a chemical compound, but a mechanical mixture of oxygen and nitrogen gases, inasmuch as all gaseous chemical compounds known to chemists are the results of the union of definite volumes of the primitive gases, without the occurrence of any fractional parts.

There are other arguments, however, to be adduced in favour of the mechanical union of oxygen with nitrogen in atmospheric air. Some of the most weighty are as

follow :—The act of chemical combination between two bodies is generally attended by some notable change of temperature; but no such change is recognisable on mixing oxygen and nitrogen gases in the proportion necessary to form atmospheric air. The result of chemical union again is generally, if not always, a body differing in one or more characteristics from the constituents entering into it; but the properties of atmospheric air may be correctly described as a mean of the properties of each. But, perhaps, the most powerful argument in favour of the mechanical nature of atmospheric air is the following :—Both oxygen and nitrogen gases are slightly soluble in water, as is well known; but although atmospheric air is said to be also soluble to a slight extent in water, this statement, to be quite correct, must be a little modified. Careful analysis of the gaseous matter absorbed by water proves its composition to be—

Oxygen	32·00
Nitrogen	68·00

Whereas, if atmospheric air were absorbed in the strictest sense of the expression, the composition should be—

Oxygen	20·90
Nitrogen	79·10

If atmospheric air be not a chemical compound of oxygen and nitrogen, but a mere mechanical admixture, some explanation is necessary of the cause which maintains them in such perfect homogeneity; for though it be true that the difference of specific gravity between oxygen and nitrogen gases is only slight, yet that difference should suffice to determine their separation, according to the ordinary laws of gravity as evidenced by solid and liquid bodies. Whatever may be the ultimate cause of it, the phenomenon of gaseous diffusion is now well recognised as something distinct from chemical attraction. A striking experiment, illustrative of this property, was performed by Dalton. This philosopher took two cylindrical vessels, one of which was filled with carbonic acid, the other with hydrogen gas; and the latter being placed uppermost, a communication was established between them. Notwithstanding the great difference between the specific gravity of hydrogen and carbonic acid—the latter being twenty-two times heavier than the former—perfect admixture will speedily ensue.

Dr. Dalton explained this phenomenon by the assumption that the particles of one gas manifested an attraction for the particles of all other gases, with the exception of itself—according to which supposition one gas may be regarded as being a vacuum to another, a deduction which accords sufficiently well with observed phenomena, though it fails to assign their cause.

To Professor Graham we owe the fullest exposition which has been made of the law of diffusion of gases. His experiments and deductions have already been given in a former part of this treatise (page 176).

Extent of the Atmosphere.—The atmosphere is not of equal density throughout. This follows of necessity, seeing that its lower strata have to bear the superincumbent weight of all above. The most direct means of proving the increasing rate of atmospheric attenuation upwards, is by noticing the fall of a column of mercury in the barometer, the nature and construction of which will be soon explained. Much speculation has arisen concerning the distance from the earth's surface to which the atmosphere extends. Some philosophers have advocated the opinion that the progressive attenuation upwards is infinite, and that it consequently pervades all space; but the most prevalent idea is that it does not extend farther than forty-five miles. In

the "Philosophical Transactions" for 1822, there is a paper by Dr. Wollaston on the finite extent of the atmosphere, in which the hypothesis embodied in the title is argued with much ingenuity. If the atmosphere be supposed infinite, it should pervade all space, and the heavenly bodies should each attract a portion commensurate with their own *mass* or gravitating power. But certain astronomical observations made by Dr. Wollaston and Captain Kater are in favour of the conclusion that there is no solar atmosphere; and the observations of other astronomers render the supposition probable that the planet Jupiter has no atmosphere. These deductions, if correct, are evidently opposed to the hypothesis of infinite atmospheric subdivision. Dr. Wollaston, then, was strongly of opinion that our atmosphere is limited, and he accounted for the limitation thus:—He imagined that at a certain height the repulsive power subsisting between the gaseous particles of the atmosphere was exactly balanced by their gravitating power, and that the balance thus established determined the range of atmospheric action.

The student will not fail to remark that the hypothesis of Dr. Wollaston is only tenable on the assumption of the atomic state of matter; in favour of which it is indeed cited as a powerful argument. The atmosphere can only be limited by the causes just assigned, at least concomitantly with, and as the result of, an atomic constitution. If, therefore, the atomic constitution of oxygen, nitrogen, carbonic acid, and the adventitious elements of the atmosphere be granted, the strongest probability arises that every description of matter is similarly circumstanced. It must be admitted, however, that although astronomical observations may be conclusive against the presence of an atmosphere around the sun and Jupiter, and must be, therefore, accepted as a proof that our own atmosphere is limited in extent, the reasonings of Dr. Wollaston in this matter are divested of one important element. That philosopher takes cognizance alone of the limitation of gaseous bulk as the result of diminished pressure; but diminished temperature plays, at least, an equally important part towards the same result. Between gases, commonly so understood, and vapours, there is no absolute difference whatever; the difference is purely of degree. Now vapours are condensable into liquids and solids by cold alone, and extreme cold is a powerful agent towards effecting the artificial condensation of gases. Given, therefore, a sufficient amount of cold, there seems no reason why the atmospheric limit may not be determined by the operation of this cause. Now, in proportion as we ascend above the earth's surface, the degree of cold increases. This is demonstrated by the existence of snow on elevated mountains, and is readily accounted for. Gaseous matter is not heated by the sun's direct rays, or by any radiant heat whatever—it derives its temperature from direct contact with heated bodies; and hence the amount of that temperature will always be proportionate with the heated mass with which it is in contact. Now, inasmuch as the mass of a mountain is but trifling in comparison with the general mass of our globe, we have a cause for the low temperature of these elevated regions. Another circumstance, however, contributes to the same effect. The specific, or non-evident, heat of a given volume of attenuated gas is greater than the specific heat of the same amount compressed; hence the temperature of a definite volume of rarefied atmospheric air is less for equal increments of heat than if the same weight of air were condensed into a smaller volume. So far as our observations have extended, the decrease of temperature is equal to about one degree of Fahrenheit's scale for every 300 feet of elevation. Probably the rate of decrease is still more considerable at higher elevations.

The Barometer.—In the early part of the seventeenth century the pressure of the atmosphere was first noticed by Galileo; but the barometer, an instrument for

demonstrating the variation of this pressure, is referable to his pupil Torricelli. The barometer, in its simplest form, is made as follows:—Procure a piece of thick glass tubing, having an internal diameter not less than a fourth of an inch—if more all the better—and about thirty-four or thirty-five inches long. Seal one end of the tube hermetically by the blow-pipe flame, allowing the other extremity to remain open. Next, holding the open extremity of the tube uppermost, fill it with mercury, place the thumb on the mercury, and invert the tube, mouth downward, into a small basin or dish, also containing mercury. These dispositions being made, it follows that the length of the column of mercury capable of being supported in the tube will be proportionate to the amount of atmospheric pressure on the surface of the mercury contained in the basin.* The length of this column is subject to variation from day to day, but it will generally be comprised within a small range above or below thirty inches. Supposing the atmospheric pressure at the time of the experiment just detailed to be equivalent to thirty inches of mercury, and the tube to be thirty-four inches long, then it follows that the original mercurial column will sink to the extent of four inches on inverting the tube; leaving a seemingly empty space, to which the appellation of Torricellian vacuum has been applied. It is not, however, a vacuum, but filled with the vapour of mercury.

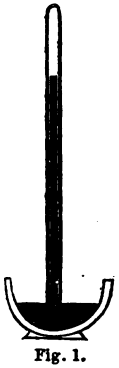


Fig. 1.

The instrument just described, and a section of which is given in Fig. 1, is the simplest, and perhaps most correct form that the barometer can assume. The disposition of parts is, however, so inconvenient that a modification is generally introduced.

In common barometers the modification is usually of the kind depicted in Fig. 3. The open extremity of the tube is bent upwards, and blown into a little bulb, through one side of which there is an aperture, *a*, opening a communication with the external atmosphere. It is more usual, however, in delicate barometers to dispense with this bulb, as represented in Fig. 2. This construction enables the observer to read off exactly the number of barometric inches and parts of inches by a suitable scale appendix, counting from the level *l*, at which the mercury stands in the short leg of the tube.

Fig. 2.

Fig. 3.

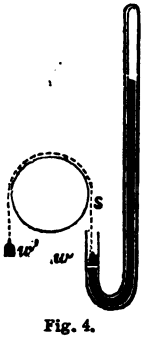


Fig. 4.

Though the real function of the barometer is to indicate the degree of atmospheric pressure at any time, it is applied to a useful collateral purpose—namely, to the purpose of indicating changes of weather. Practically it is found that certain conditions of atmospheric pressure co-exist with rain, wind, and drought; the barometer indicates these conditions, and thereby becomes a *weather-glass*. Occasionally the barometric weather-glass is supplied with a dial index, the motion to which is given in the following manner:—A small light pulley-wheel is attached in such manner to the instrument that by means of the weights *w w'* (Fig. 4), and a connecting string, *s*, the wheel shall turn by the upward pressure of mercury against the weight *w*, and

* *About 15 lbs. to the square inch.*

return by the slightly preponderating weight of *w* over *w'*, when the mercury sinks in the short leg of the syphon. This form of barometer, although convenient as a *weather-glass* for general reference, is by no means so correct as those with vertical scales, and without the wheel appendage.

Many circumstances to which no reference has been made require attention in the manufacture of correct barometers. It is of the utmost importance that the mercury employed be quite pure, and that the barometer tube neither contain moisture nor atmospheric air. Moreover, it is almost unnecessary to state that the internal diameter of the barometer tube should be of the same length throughout. The absence of moisture can be certified by drying the tube immediately before closing it; but there is only one method of totally dispelling every trace of atmospheric air—namely, by boiling the mercury after it has been poured into the tube. This operation involves much danger to the instrument, as may be readily inferred, and, consequently, adds much to its expense. Much needless inaccuracy is conferred upon ordinary barometers by forming them of tubes too small. This is done from motives of economy; to diminish the amount of quicksilver used in filling them; but the economy is misplaced. To be a correct indicator of atmospheric pressure, the mercurial column should be totally deprived (if possible) of all frictional interference. This is obviously impossible: between the glass and the mercury friction there must be; but by employing tubes of small diameter the amount of friction is needlessly increased; moreover, the surface of the mercury in them is so convex that its correct level is difficult to be ascertained. A moderately correct barometer cannot be dispensed with by the chemist who conducts experimental researches on gaseous bodies. He cannot depend from day to day on the continuance of any given amount of atmospheric pressure, consequently the gaseous mixtures upon which he operates will be continually changing their volume. The law of increase or decrease of volume, however, for any given rate of pressure is well known; and the chemist can, therefore, reduce a given volume at one temperature to the hypothetical volume at another temperature with facility by the application of the rules previously explained in a former part of this treatise (page 112).

Combinations of Oxygen with Nitrogen.—There are five known combinations of oxygen with nitrogen, constituting the following bodies:—

	Atoms.		Parts by Weight.		Symbol.
	N.	O.	N.	O.	
1. Protoxide of nitrogen	1	1	14	8	NO
2. Binoxide of nitrogen	1	2	14	16	NO^2
3. Hyponitrous acid	1	3	14	24	NO^3
4. Nitrous acid	1	4	14	32	NO^4
5. Nitric acid	1	5	14	50	NO^5

General Remarks.—The list of compounds of oxygen with nitrogen presents the example of a complete series so far as it extends, and for this reason it well illustrates the philosophy of the atomic theory. Except the last (nitric acid), none of the preceding compounds occur in nature; and even nitric acid, though it does naturally exist, is always found in combination usually with potash or soda, the nitrates respectively of these alkalies. Nitrate of potash is commonly known by the appellation of nitre, or saltpetre; hence the terms nitric acid and nitrogen. Although in the foregoing tabular view the compounds of oxygen with nitrogen are necessarily arranged

in the numerical order of their constituents, nevertheless, in describing them, this order should be departed from; nitric acid, *the last*, being the first discussed, because from nitric acid all the others are prepared, directly or indirectly.

Nitric Acid.—This acid is usually regarded as synonymous with *aqua-fortis*, a combination of the real or anhydrous nitric acid with water. Since, however, Deville has succeeded in isolating the real or anhydrous nitric acid, the two should not be confounded.

Real or Anhydrous Nitric Acid.—This compound was isolated not long ago by M. Deville, who succeeded in obtaining it by passing a slow current of chlorine first over chloride of calcium and sulphuric acid, and subsequently over dry nitrate of silver, previously heated to 203° F., and maintained during the operation at a temperature of 136° to 150° F. The results of decomposition were caused to pass through a U-tube, cooled down to — 5 5° F. Chloride of silver resulted, oxygen gas escaped, and nitric acid, deprived of water, was obtained in crystals. At the same time, portions of a volatile liquid—most probably nitrous acid—escaped.

Anhydrous nitric acid is stated by Deville to consist of brilliant colourless rhombic prisms, which fuse at 84° or 86° F., and boil at 113° to 122° F., suffering decomposition at the latter temperature. The crystals manifest a remarkable tendency to combine with water, hydrated nitric acid being the result.

Hydrated or Hydrous Nitric Acid—Aqua-fortis.—This compound is prepared by subjecting to distillation a mixture of sulphuric acid and nitrate of potash (nitre), or nitrate of soda. The theory of the decomposition which ensues is exceedingly simple. Nitric acid has less *affinity* (to use a common but not quite correct expression, *vide pp.* 54 *et seq.*) for potash or soda than is possessed by sulphuric acid for the same; for which reason double decomposition ensues—nitric acid united with water being evolved, and a combination of sulphuric acid with potash or soda remaining. The combination in question may be a sulphate, or a bi-sulphate, or, lastly, a mixture of the two, as we shall learn presently.

There are two combinations of sulphuric acid with potash—the neutral sulphate and the bi-sulphate. The first of these is anhydrous (devoid of water), and consists of one equivalent of sulphuric acid, 40, united with one equivalent, 48, of potash; the bi-sulphate of potash, on the contrary, is the result of union between two equivalents of sulphuric acid, one of potash and one of water. Anticipating the preparation of oil of vitriol (sulphuric acid), it will be necessary here to mention that the strongest oil of vitriol of commerce is composed of one equivalent of sulphuric acid and one of water; consequently, inasmuch as nitric acid rapidly decomposes if it do not find a certain minimum of water wherewith to combine, the quantity of oil of vitriol employed in the manufacture of acid requires to be nicely apportioned, if the operator wishes to produce the maximum quantity of aqua-fortis of the maximum strength. The best practical quantities for affording this result are 100 nitrate of potash, and 98·8 oil of vitriol—proportions which yield 125·71 parts of bi-sulphate of potash and 62·29 of monohydrate of nitric acid, which is the strongest form that aqua-fortis can assume.

Monohydrate of nitric acid, as its name indicates, is a compound of one equivalent (54) of nitric acid, and one equivalent (9) of water; or, in other terms, it contains about 14 per cent. of water. Its density is about 1·522, and its boiling point is about 186·8° F. The monohydrate of nitric acid solidifies at about 58° F. It is nearly colourless when pure; but on account of a tendency to decomposition, it assumes a tint more or less yellow from the operation of slight causes, such as the influence of heat or light,

especially the direct solar rays. Monohydrate of nitric acid manifests a strong tendency to unite with water, with which it seems to combine in all proportions; but great probability attaches to the opinion that the seemingly innumerable combinations of nitric acid and water are really mixtures of various definite hydrates of that acid. The existence of one hydrate we have already proved. There is yet another, far more stable than the last, commonly known to chemists; and various considerations point to the existence of others which have not been isolated. Owing to the tendency which monohydrate of nitric acid displays to unite itself with water, and reach a higher state of hydration, it seeks out aqueous vapour, floating invisibly in the atmosphere, and, by union with it, generates cloudy fumes: hence the appellation "*fuming nitric acid*," by which it is often designated.

The second hydrate of nitric acid which has been isolated is a compound of one equivalent real nitric acid and four of water: hence its formula is $NO^5 + 4HO$. It may be procured by adding a suitable quantity of water to the proportions of oil of vitriol and nitrate of potash, already given when describing the manufacture of the protohydrate; but the process most instructive to the chemical student consists in mixing a portion of the protohydrate with an excess of water, and subjecting the mixture to distillation.

In performing the above operation the retort should be tubulated, and furnished with a thermometer, for the purpose of indicating the changes which ensue. For some time after the application of heat, water almost pure will come over, the thermometer continuing to indicate 212° F. (the boiling point of water). Soon, however, the temperature will begin to rise, and it will continue rising until about 253° F., when, becoming stationary, it will continue so until the end of the operation. Concomitantly with this steadily-maintained temperature, a combination of nitric acid and water, having one definite strength, will pass over; it consists of four equivalents of water, united with one of real nitric acid.

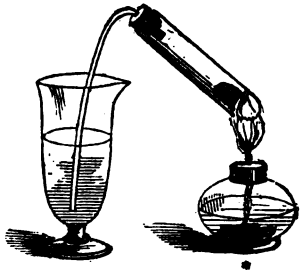
This hydrate possesses a far more stable composition than the one already described. It may be distilled many times successively without incurring decomposition, or exposed to the direct solar rays for an indefinite period with similar absence of effect.

Chemical Qualities and General Characteristics of Nitric Acid.—The most striking characteristic of nitric acid, and the one upon which its most important applications depend, is the large amount of oxygen (5 equivalents) which it contains, and the facility with which that oxygen is imparted to other bodies having an affinity for it.

Dependent upon this quality of nitric acid is a frequent application of it, in the course of analysis and chemical manufacture, as an oxidizing agent. Dependent also on the same quality, though somewhat more remotely, is the employment of nitrate of potash (nitre) in the gunpowder manufacture. Nitre contains not only the portion (five equivalents) of oxygen due to the presence of nitric acid, but one equivalent in union with potassium to form potash. Nitrate of potash, therefore, contains six equivalents of oxygen in all. Hence it follows, therefore, that if nitrate of potash be intimately mixed with bodies having the property of burning in oxygen, we obtain a mechanical compound which can burn, independently of the presence of atmospheric air. Of this kind is gunpowder. If the student will now turn to page 283, in which the process is given for preparing oxygen gas by distillation from chlorate of potash, he will at once perceive that nitric acid, in its composition, presents a striking analogy to the chloric acid; and, moreover, that nitrate of potash is the exact counterpart of

chlorate of potash, merely substituting nitrogen for chlorine. Not only is there a similarity of composition, but a similarity of properties also between the nitric and the chloric acids—the nitrates and the chlorates respectively. As it is always desirable to let no opportunity escape of impressing generalizations on the mind, the student will do well to remember that chloric, nitric, iodic, and bromic acids, constitute a well-marked group; and, moreover, that there also exists an equally marked series of analogies between their combinations. If an unknown acid yields, on combination with an alkali, or other base, a salt capable of forming touch-paper, the salt in question must be either a nitrate, chlorate, iodate, or bromate; and must contain either the nitric, chloric, iodic, or bromic acid. Nitric acid may be individualized by the following characteristics:—If uncombined with a base, and moderately concentrated, it tinges the skin, and animal substances generally, deep yellow; hence it is sometimes employed as a dyeing agent. This indication of nitric acid is exceedingly valuable when the substance has been administered criminally. Frequently the characteristic just indicated will be sufficient as a qualitative test of nitric acid. Should there remain any doubt, however, the following plan may be adopted:—

Take a test-tube, fit to it accurately a cork and bent delivery-tube, passing into a solution of proto-sulphate of iron (green vitriol). The arrangement having been duly made, place a few shreds of copper turnings in the test-tube, pour upon it the suspected acid, and apply heat. If the solution of proto-sulphate of iron turn black, the acid employed is the nitric. The *rationale* of this operation will be made known under the head of binoxide of nitrogen.



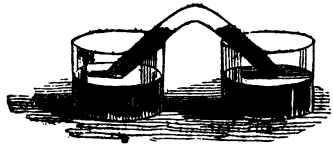
Quantitative Determination of Nitric Acid.—Chemists are not aware of any test endowed with the property of combining with nitric acid, and forming an insoluble precipitate; the quantity of this acid present in aqueous solution—*provided no other matter be there*—may be readily ascertained thus:—Weigh a given quantity—say 200 grains—of the acid solution into a glass-flask, dilute with water, and add a known quantity of oxide of lead; it should be sufficient not only to combine with the whole of the acid present, but to leave a portion in excess. The flask, now containing nitric acid, oxide of lead, and water, is to be exposed to heat, which will drive off all the water, and leave a mixture of nitrate of lead with oxide of lead behind. If the flask be now weighed again, a certain loss will be appreciable—that loss proportionate with the amount of water originally combined with the nitric acid. This operation is founded on the circumstance that nitrate of lead is an anhydrous salt—in other words, a salt, into the constitution of which water does not enter.

Composition of Nitric Acid demonstrated.—The composition of nitric acid may be proved both analytically and synthetically. The synthetical method consists in exposing a mixture of oxygen and nitrogen gases in contact with water; or, still better, an alkaline base to the agency of electric sparks. If a mixture of oxygen and nitrogen gases, in known proportions, be employed, the condensation ensuing will be found to correspond with one equivalent (14 parts by weight) of nitrogen, and five equivalents (40 parts by weight) of oxygen. The condensation is due to the formation of nitric acid; and on its union with water, or a base of the latter, it will be found capable of

making touch-paper; hence, considering the limitation of the experiment, it must be a nitrate, and its acid, consequently, the nitric acid.

Although it is necessary to mix the two gases, in the proportion of the composition of nitric acid, if the operator desire to obtain the maximum amount of that acid from the minimum amount of gaseous mixture,—nevertheless, portions of nitric acid are generated, whatever the relation subsisting between the two gases may be. Thus, for example, atmospheric air answers perfectly well; the combination of nitrogen with oxygen ensues, and nitric acid is formed. Hence we are at no loss to account for the production of nitric acid in nature, and for the frequent presence of nitrate of ammonia in rain-water.

The annexed cut represents a convenient apparatus for effecting the combination between oxygen and nitrogen gases. A glass tube, open at both ends, is bent into an obtuse angle. The angular part contains the mixture of oxygen and nitrogen, in contact with water, or a basic solution, and each end terminates in a vessel of mercury. The manipulative process has been in such manner conducted that a quantity of mercury is allowed to remain in the tube, leaving a space between its two surfaces, across which electric sparks from a moderately-powerful machine can dart with ease. Inspection of the diagram will make evident, that on establishing electric communication with the two vessels, a current of sparks will rush through the intervening space containing the mixed gases.

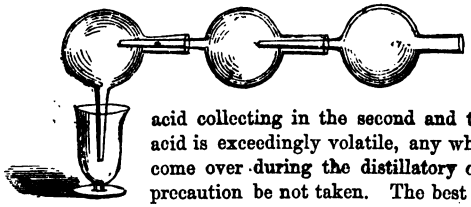


Analytically, the composition of nitric acid may be determined by decomposing nitrate of lead in a tube heated to redness, transmitting the evolved vapour through copper turnings, also heated to redness, and collecting the final gaseous results. The latter will be nitrogen acid, in such proportion that every equivalent, or 14 parts by weight, of it must have been in combination with five equivalents, or forty parts by weight, of oxygen.

Determination of the presence of Nitric Acid in combination with bases.—Inasmuch as all nitrates are decomposable by the united influence of sulphuric acid and heat, the process already given for distinguishing the presence of uncombined nitric acid requires to be modified thus:—Mix the suspected nitric acid compound with a few shreds of copper turnings in the distillatory tube; add sulphuric acid, apply heat, and pass the result of distillation through a solution of protosulphate of iron. If the latter become blackened, nitric acid in combination will have been present.

Uses of Hydrated Nitric Acid (*Aquafortis*).—Not only is this liquid extensively employed in the laboratory of research, and in medicine, but it is also of very extensive use in the arts. The commercial acid is generally not quite pure. It is apt to contain iron, sulphuric and hydrochloric acids; it is, moreover, generally coloured reddish, by the presence of hyponitrous and nitrous acids, the results of decomposition of a portion of nitric acid. The latter kind of impurity is usually of no consequence, even in conducting operations of analytical delicacy; but the presence of all other impurities should be carefully guarded against. The presence of iron may be demonstrated, if it exist, by diluting the acid with water, and adding a solution of ferrocyanide of potassium (prussiate of potash). Sulphuric acid is indicated by a white precipitate *occurring* on the addition of a baryta salt solution; and hydrochloric acid by a solution

of nitrate of silver, with which it throws down a white precipitate. From iron and sulphuric acid aquafortis may be purified by slow distillation, condensing the result in a succession of receivers, as represented in the annexed cut. The iron will be wholly left behind in the retort, so in all probability will the sulphuric acid also; but should any of the latter come over, it will deposit in the first receiver, pure nitric acid collecting in the second and third. Inasmuch as hydrochloric acid is exceedingly volatile, any which may have been present will come over during the distillatory operation if a special measure of precaution be not taken. The best plan consists in adding a solution of nitrate of silver to the impure acid, and subsequently distilling. The theory of this removal will be explained under the departments of hydrochloric acid and silver.



PROTOXIDE OF NITROGEN.

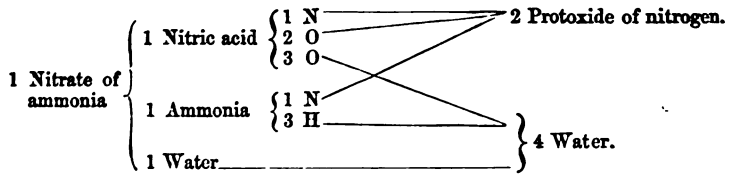
Equivalent or atomic weight	22
Atomic or combining volume	
Specific gravity	1·5246

Historical Notice and Synonymes.—Protoxide of nitrogen was discovered by Dr. Priestley, who denominated it *dephlogisticated nitrous air*. By the associated Dutch chemists it was termed *gaseous oxide of azote*. The apellation *nitrous oxide* was given by Davy, and that of *laughing gas* popularly, on account of the exhilarating effects produced by its inspiration. *Protoxide of nitrogen*, however, is its most appropriate designation.

Preparation.—Nitric acid, by acting upon metals, is invariably decomposed; but the decomposition is not always the same. In certain cases every equivalent of nitric acid loses four equivalents of oxygen, when, as a necessary consequence, protoxide of nitrogen results; in others, the absorption of oxygen is not proportionally so great, three equivalents only being removed from every equivalent of nitric acid, when, as the necessary consequence, the gas next to be described is evolved. Frequently the two gases are simultaneously generated. If zinc be the metal employed, and if the nitric acid be diluted, protoxide and binoxide of nitrogen are simultaneously evolved; but if the mixed gas be allowed to stand for some time in contact with zinc or iron filings moistened with water, the binoxide of nitrogen which may be present yields up its oxygen, and becomes reduced to the condition of protoxide.

The foregoing method of preparation, although it be instructive as illustrating the composition of the compound under notice, is not the most convenient method of preparing it. This is best accomplished by the distillation of a crystalline salt termed nitrate of ammonia. The distillatory apparatus should be a glass retort and bell-glass, or a gasometer, and the heat applied should not exceed 500° Fah.

Thus treated, the decomposition of nitrate of ammonia is complete: it entirely disappears, water and protoxide of nitrogen (the latter a gas) being the sole results. The theory of this decomposition will be readily understood by reference to the following diagram, from which it appears that one equivalent of nitrate of ammonia consists of one equivalent of nitric acid, one of ammonia, and one of water; and that it yields, by decomposition, two of protoxide of nitrogen and four of water.



Or, adopting the notation of chemical symbols, the decomposition stands thus:—

$$NH^3HO.NO^5 = 2NO + 4HO.$$

Properties.—The protoxide of nitrogen, at ordinary temperatures and pressures, is a colourless gas, considerably heavier than atmospheric air, sweetish to the taste, capable of supporting respiration for a short period, and giving rise to a kind of intoxication. It is rapidly absorbed by water, which has been previously boiled, to the extent of nine-tenths of the bulk of the water employed. Water which has thus been saturated with the gas evolves it again unchanged when heated. Protoxide of nitrogen strongly resembles oxygen in its relation of supporting combustion. A candle burns in it with a brilliant white flame and crackling noise. Before its extinction the interior flame becomes enveloped with an exterior blue one, by which characteristic it may be distinguished from oxygen. Sulphur, if introduced into this gas when feebly burning, is extinguished; but if in the state of full combustion, it burns with great vigour. Phosphorus, if ignited and immersed, burns with almost the same brilliancy as in oxygen—nevertheless, phosphorus may be heated, and even sublimed in the gas, without combustion. Red-hot charcoal burns with far greater brilliancy in protoxide of nitrogen than in atmospheric air, but not with such brilliancy as in oxygen. The results of this combustion are half a volume of carbonic acid (containing half a volume of oxygen), and one volume of nitrogen, from each volume of the protoxide decomposed. A mixture of protoxide of nitrogen and hydrogen gases detonate by the electric spark, or may be combined by the agency of spongy platinum. The result of combustion varies according to the quantity of gases mixed. When the volume of hydrogen slightly predominates, nitrogen is the sole gaseous product of the decomposition; if in lesser proportionate quantity, some nitric acid is also generated. Under a pressure of 30 atmospheres, this gas liquifies at 32° F., and at the very low temperature of — 148° F. it freezes.

Determination of Protoxide of Nitrogen.—The only gas with which it can be confounded is oxygen, with which it presents many common points of similarity. Chemical analysis is the only certain method of distinguishing the two.

Analysis of Protoxide of Nitrogen.—The simplest means of effecting this analysis is by the employment of potassium, as follows:—Having measured off, over mercury, a known volume of protoxide of nitrogen, transfer it to a small retort tube; then pass up through the mercury a globule of potassium, attached to an iron wire, and apply heat externally. Decomposition of the gas ensues. The phosphorus uniting with oxygen forms potash, and pure nitrogen remains. The tube having cooled, the gas must be transferred back to the graduated vessel in which it was measured. Its volume will not have been altered by the decomposition, notwithstanding the removal of oxygen from it. We arrive at the conclusion, therefore, that the gas contains its own volume of nitrogen.

Hence if we deduct from the weight of one volume of protoxide of nitrogen, or, in other words, the specific gravity of the gas, = 1·5246, the weight of one volume of nitrogen or *its* specific gravity, = 0·972, there remains 0·5526, which is nearly half the specific gravity of oxygen gas. Hence one volume of protoxide of nitrogen contains—

1 volume of nitrogen	0·972
½ volume (one atom) of oxygen . . .	0·5528
	1·5248

which is practically identical with 1·5246, the specific gravity previously given.

The analysis of protoxide of nitrogen may be also readily effected by the eudiometric method—namely, mixture with hydrogen and subsequent combination, either by means of the electric spark or by spongy platinum. Let us assume that the proportions of gases employed in the eudiometric determination are as follows:—

100	measures of	protoxide
150	„	hydrogen
250		

After passing the electric spark let us assume that the 250 measures have become reduced to 150, showing the disappearance of 100. It now remains to be seen how much hydrogen exists in the 150 measures of gas. The determination is effected as follows:—Introduce 50 measures of oxygen,—making 200 altogether,—and again pass the electric spark. There will now remain only 125 measures of gas, 75 measures having disappeared—oxygen and hydrogen—in the proportions necessary to form water—namely, 50 of hydrogen and 25 of oxygen. Consequently in the 150 measures of gas which remained after the first detonation, there were 50 measures of hydrogen, and, consequently, 100 of nitrogen. Now, seeing that we at first had 150 measures of hydrogen, and that 50 have been accounted for, 100 measures must have been exhausted in combining with the protoxide of nitrogen, which, therefore, are proved to contain,

100	measures of	nitrogen,
50	„	oxygen.

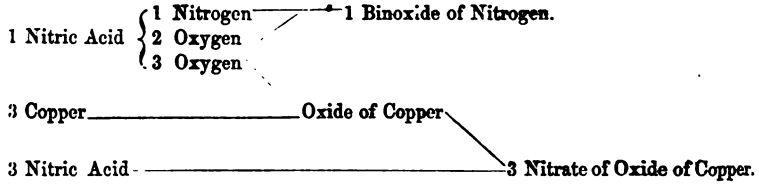
Physiological effects of the Gas.—Very soon after the discovery of this gas its property of exhilaration when breathed was remarked. The term *laughing gas*, however, popularly given to it, is so far incorrect, that laughter is by no means a universal result of its inhalation. The effect produced is a transient intoxication, during which various phases of character manifest themselves—the tendency to fight being at least as usual as the tendency to laugh.

BINOXIDE OF NITROGEN.

Equivalent or atomic weight	30
Atomic volume	[ ][ ]
Specific gravity	1·0395

Historical Notice and Synonymes.—This combination of nitrogen and oxygen was discovered by Hales, but first carefully studied by Priestley. In addition to the term binoxide of nitrogen, by which I have denominated it, the combination is also known as *deutoxide of nitrogen*, *nitrous gas*, and *nitric oxide*.

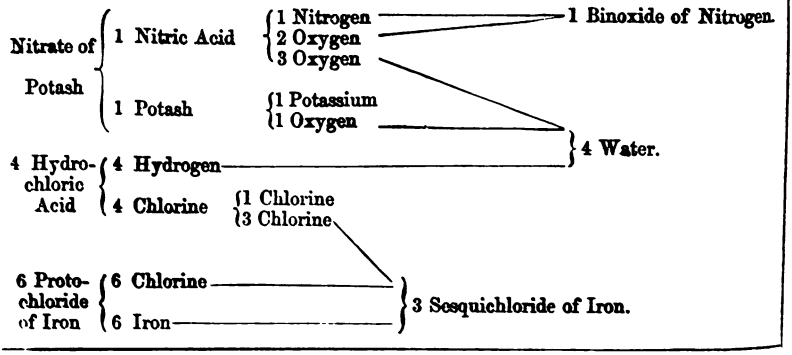
Preparation.—The simplest and most usual method of preparing this compound consists in the decomposition of nitric acid by certain metals, of which copper is perhaps the most eligible. To insure purity of the gas by this operation, it is necessary that the nitric acid be considerably diluted, and that the mixture be kept cool during the evolution of gas. The decomposition which ensues is illustrated by the appended diagram :—



This, although the usual process had recourse to for the generation of binoxide of nitrogen, is very apt to develop the gas in the condition of slight impurity. For all ordinary purposes, this is immaterial; but when extreme purity is required, the best process for manufacturing binoxide of nitrogen consists in heating nitrate of potash with a solution of protochloride of iron in an excess of hydrochloric acid.

Before describing the decomposition, which is somewhat more complex than any which have come under our notice hitherto, I must premise a few explanations. Protochloride of iron is employed in the decomposition; and we shall presently observe that the protochloride will be converted into the sesquichloride of that metal. The expressions *proto*-chloride and *sesqui*-chloride must therefore be well understood. Protochloride of iron is a union of chlorine with iron in the first grade of chlorination. It is made up of one equivalent of chlorine in union with one equivalent of iron. There is yet another compound of these elements, in which the proportion of chlorine is greater,—the greatest portion, in fact, which a given weight of iron is able to combine with. Hence it is sometimes called the *per*-chloride of iron, from the Latin *per* (very much); but the term *sesqui*-chloride is more eligible (*sesqui*, one and a-half), because it indicates the exact ratio. Sesquichloride of iron is a compound of two equivalents of iron, in union with three equivalents of chlorine, thus, (Fe^2 $Cl.^3$), which is the ratio of 1 : 1½.

The decomposition will be rendered more intelligible by means of a diagram.



Or the same decomposition is indicated by symbolical notation as follows :—

$$6Fe\,Cl + KO\,.\,NO5 + 4H\,Cl = NO2 + 3\,(Fe^2\,Cl^3) + K\,Cl + 4HO.$$

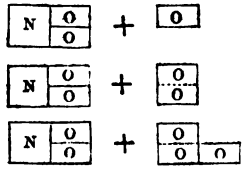
The prochloride of iron employed in the decomposition is thus prepared :—Take two volumes of hydrochloric acid. Heat one with iron filings until no more of the latter will dissolve; we thus obtain a solution of protochloride of iron; finally, add to the mixture thus obtained the second volume of acid. The solution is now ready for incorporation with nitrate of potash.

Properties.—Binoxide of nitrogen, whichever process be adopted, is liberated in the state of a colourless gas, devoid of both acid and alkaline qualities, and of ordinary combustible properties. It may be collected either over mercury or water, notwithstanding that one-twentieth is dissolved by pure recently boiled water.

When allowed to come in contact with atmospheric air or oxygen, ruby-red vapours of hyponitrous and nitrous acid result, which are rapidly absorbed by water. This property of binoxide of nitrogen induced Priestley to employ it as an agent for eudiometric purposes. It is, however, an incorrect method, because hyponitrous and nitrous acids—occasionally also nitric acid—being generated in variable proportions, the amount of condensation is scarcely ever the same for any two consecutive experiments. This may be illustrated by the following scheme :—

Binoxide of Nitrogen,

By combination with different amounts of oxygen, binoxide of nitrogen is converted into hyponitrous and nitrous acid, and nitric acid, respectively. The exact amounts of oxygen required for this purpose are as follows :—



= Hyponitrous Acid.

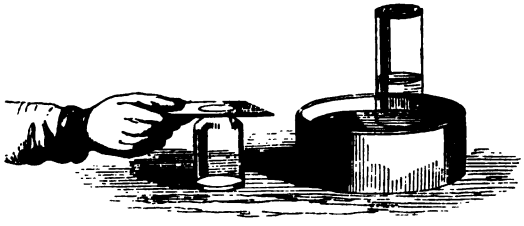
= Nitrous Acid.

= Nitric Acid.

Priestley was the first who suggested the employment of binoxide of nitrogen as an eudiometric agent. He was unaware of the indeterminate nature of the resulting combinations, and assumed that every volume of the binoxide was rendered capable of absorption by water by the addition of one-fourth its own volume of oxygen exactly; in other words, he assumed that hyponitrous acid was the sole result of combination. If this condition could be universally depended upon, the total amount of oxygen contained in any gas might be determined by adding binoxide of nitrogen until ruby-red vapours ceased to appear, waiting until absorption had been perfected, and dividing the amount of gas lost by absorption by four.

It remains now to state that, amongst the conditions which interfere with the rate of absorption, the following are well recognized :—Amount of agitation to which the two gases are subjected—rapidity of mixture—opposite conditions of mixture, such as

whether the binoxide be added to the air, or other oxygenous gas, or the latter to the binoxide—relative proportions of the two gases—heat of the mixture.



The abstraction of oxygen gas by means of binoxide of nitrogen can be easily conducted as follows:—On the shelf of a pneumatic trough invert a jar containing atmospheric air. Let the exact space filled with the atmospheric air be indicated by a file scratch, and let it be regarded as constituting one volume. Let there be provided a second jar or bottle, the contents of which, when closed with a glass valve, are equal to the volume marked off in the first. Fill the second with binoxide of nitrogen, and add it to the atmospheric air confined in the first, when red vapours will appear, and, becoming absorbed, the resulting gaseous contents will not fill two volumes, by some variable quantity dependent on the relative amounts of hyponitrous and nitrous acid formed.

An ignited match or taper plunged into binoxide of nitrogen is extinguished; so is burning charcoal, except its combustion at the instant of immersion be intense, under which condition it burns with increased splendour. Ignited sulphur is at once extinguished when plunged into a vessel containing this gas, and phosphorus may be sublimed in an atmosphere of binoxide of nitrogen without burning. If, however, phosphorus already well ignited be immersed, the combustion is very intense. These experiments strikingly illustrate the power of chemical decomposition in modifying the character of bodies. Binoxide of nitrogen contains twice as much oxygen as protoxide, and yet it does not support combustion with equal facility. Binoxide of nitrogen is absorbed with great facility by a solution of protosulphate of iron, forming a liquid the exact composition of which has not been determined. It rapidly combines with oxygen gas, as we have seen. Nitric acid also dissolves a considerable quantity of the gas, and then becomes a coloured liquid, sold in commerce under the appellation of nitrous acid; it is very different, however, from the true chemical nitrous acid presently to be discussed. The changes effected on nitric acid by the absorption of binoxide of nitrogen have been well studied. They are as follow:—A portion of the binoxide, by its tendency to combine with oxygen, receives from nitric acid a portion of this element; thus giving rise to two portions of nitrous acid—one from the nitric acid deprived of a part of its oxygen, the other from the binoxide employed converted to a higher state of oxygenation. The mutual reaction of nitric acid and binoxide of nitrogen only takes place when the nitric acid employed is concentrated above a certain grade, and the colour of the result varies according to the strength of the nitric acid. Monohydrate of nitric acid gives rise to a liquid which is brown. A slight amount of dilution produces a yellow tint; and when the nitric acid employed obtains a specific gravity of 1·35, the result of passing binoxide of nitrogen through it is green. When the specific gravity of the nitric acid is still further lowered by dilution, binoxide of nitrogen no longer gives rise to an alteration of tint.

Analysis of Binoxide of Nitrogen.—(1). By heating it with potassium in a curved tube retort, as was done in effecting the analysis of protoxide of nitrogen (page 320), by

which operation the resulting gas is found to occupy half the space of the original binoxide; hence one volume of binoxide contains half a volume of nitrogen.

Subtracting from the specific gravity of the binoxide . .	1·039
Half the specific gravity of nitrogen	0·486
There remains	0·553

which is very near half the specific gravity of oxygen gas.

One volume of binoxide of nitrogen therefore contains

	Specific gravity.
½ volume of nitrogen	0·486
½ volume of oxygen	0·552
	1·038

without condensation; from which circumstance we infer that the combining or atomic volume of the binoxide is [|]

(2). By admixture with hydrogen, and subsequent explosion in a eudiometer.

Equal volumes of binoxide of nitrogen and hydrogen being mixed and exploded, the result is water and nitrogen, as represented by the annexed diagram.

Binoxide Nitrogen	N	O_2	when inflamed produce	Water and	
Hydrogen	H	H			N

Hence the composition of the binoxide of nitrogen is

			Atoms.		Atomic weight.
N	O	or, Oxygen	2	=	16
	O	Nitrogen	1	=	14
					30 Atomic weight of Binoxide.

We have already deduced the specific gravity of the binoxide by one form of calculation. We may check that result by adopting another form, the principles of which have been described at page 171.

$$\frac{\text{Specific gravity of hydrogen.} \times \text{Atomic weight of binoxide.}}{2} = \text{Specific gravity of binoxide.}$$

$$\frac{0693 \times 30}{2} = 1{\cdot}0395$$

HYPONITROUS ACID.

Equivalent or atomic weight . . . . . 38.

History and Synonymes.—The existence of this compound was inferred by Gay Lussac, who concluded from his experiments* that a compound of nitrogen and oxygen exists intermediate between binoxide of nitrogen and nitrous acid. He mixed binoxide of nitrogen and oxygen together, in tubes standing over mercury, and containing some concentrated solution of potash, and found that under these circumstances four volumes of binoxide of nitrogen were condensed by one of oxygen. Now four volumes of the binoxide contain two volumes (equal to two atoms) of nitrogen, and two volumes (equal to four atoms) of oxygen. Add to these one volume or two atoms of oxygen, and we

* "Annales de Chim. et Phys.," I., 399.

have a compound of six atoms oxygen, and two nitrogen; or, halving the numbers, three atoms oxygen and one of nitrogen. This is the composition of hyponitrous acid, termed by Graham, in England, and the greater number of chemists abroad, azotous, or nitrous acid.

Preparation.—The most convenient method of generating hyponitrous acid consists in passing through a U-tube—cooled by some refrigerating mixture, such as ice and snow—a current of mixed gas, composed of binoxide of nitrogen and oxygen, in the theoretical proportions for generating hyponitrous acid—namely, four volumes of binoxide of nitrogen and one volume of oxygen. Hyponitrous acid condenses in the U-tube, under the form of a blue liquor. A portion of nitrous acid is also produced during this operation; and if the theoretical amount of oxygen gas be increased, the quantity of nitric acid generated is still more considerable.

Properties.—Hyponitrous acid, on account of the extreme facility with which it decomposes, has been only imperfectly studied free and unmixed with other nitrogenous compounds. Owing to this facility of decomposition, its atomic or combining volumes, and, consequently, its specific gravity, are unknown. Although difficult to procure in a state of isolation, hyponitrates (combinations of hyponitrous acid with bases) are obtained with moderate facility. Hyponitrate of potash is one of the most easily prepared. We have already seen that nitric and chloric acid, also nitrates and chlorates, are respectively similar; we have also seen that chlorate of potash, subjected to a sufficient amount of heat, is decomposed, chloride of potassium being the fixed or solid result, and oxygen being evolved. Nitrate of potash also yields oxygen when similarly treated; but the scheme of decomposition is different, owing to the want of affinity between nitrogen and potassium. If nitrate of potash be cautiously heated in a retort of green, or hard German white glass, pure oxygen is evolved; if the heat be, however, increased, then, towards the latter period of the operation, a mixture of nitrogen with oxygen is the result. During the period when oxygen alone is evolved, the decomposed nitrate of potash becomes hyponitrite of potash; and if the distillation be cautiously regulated, stopping it before the evolution of nitrogen, the solid matter remaining in the retort consists chiefly of hyponitrite of potash. Now, inasmuch as hyponitrite of potash is soluble in alcohol, and nitrate of potash is insoluble in that menstruum, we have a ready means of separating the two. Or we may precipitate the hyponitrous acid by nitrate of silver, with the oxide of which metal it forms a white insoluble compound.

NITROUS ACID.

Equivalent or atomic weight	46
Atomic or combining size	[ ][ ][ ]
Specific gravity	1593

Synonymes.—Hypoazotic or hyponitric acid.

Preparation.—It has already been remarked that when binoxide of nitrogen is transmitted through concentrated nitric acid, absorption of the gas takes place, accompanied with decomposition of a portion of the nitric acid, the remaining portion acquiring a red colour. Nitric acid thus affected is the nitrous acid of commerce. In addition to the artificial process of manufacturing it, as just described, it is frequently the result of the ordinary process of manufacturing aquafortis, especially towards the end of that operation. If aquafortis of this kind be cautiously distilled, and the

products of distillation passed through a U-tube, maintained cold by means of ice, a considerable amount of nitrous acid will be condensed; but a still better method of preparing it consists in the distillation, in a small German glass retort, of the salt *nitrate of lead*, previously well dried. The retort should be connected, as just described, with a U-tube recipient, maintained cool by means of a freezing mixture.

Properties.—An orange-coloured liquid, having a density of 1·42. It boils at 37·4° Fah., and solidifies at the temperature of — 7·7° Fah. Its vapour is intensely red, and has a density or specific gravity of 1·72. Although the specific term *nitrous acid* is applied to this compound, yet it can scarcely be considered an acid in the strict logic of chemistry, seeing that it does not combine with bases. If potash, or soda, or basic substances generally, be brought into contact with it, instead of directly combining it decomposes, and yields a mixture of *hyponitrite*, and *nitrate* of the base. Hence some chemists regard it as a combination of *nitric* with *hyponitrous* acids; or as isomeric* with monohydrate of nitric acid, the one atom of water in which has been replaced by an atom of hyponitric acid. In point of fact, nitrous acid is readily decomposed by contact with warm water, hydrated nitric acid and hyponitrous acid being the results. Nitrous acid is so far from being really an acid that it acts the part of a weak base to many acid bodies. For instance, it may be caused, by a peculiar treatment, to combine with sulphuric acid.

Combinations of Hydrogen with Nitrogen.—It is probable that hydrogen and nitrogen unite in four different ratios, giving rise to four distinct bodies, as follows:—

Imidogen	NH	Ammonia	NH_3
Amidogen . . .	NH_2	Ammonium . . .	NH_4

The existence of all, except *ammonia*, however, is hypothetical, neither of them being capable of isolation. Ammonia will first claim our attention.

AMMONIA.

Equivalent or atomic weight	17
Atomic size	
Specific gravity	0·5902

History and Synonymes.—The knowledge of ammonia as a separate agent belongs to a period of modern chemistry; but certain of its combinations, especially the hydrochlorate (sal-ammoniac), were known at a period of very high antiquity. Ammonia was formerly denominated the volatile alkali—a name which is still occasionally employed.

Preparation.—By applying heat to a mixture of one part pulverized sal-ammoniac and two parts quicklime: both by weight. The operation may be conducted in a glass retort, or flask, and the resulting ammonia (a gas), if required absolutely free from atmospheric air, must be collected over mercury.

* ισος *equal*, μερος *part*, having an equal number of parts.

The decomposition is as follows :—

Hydrochlorate of Ammonia { Ammonia . . . . . *escapes*
Hydrochloric acid { Hydrogen
Chlorine

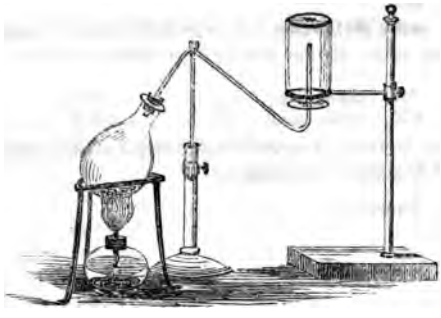
Lime . . . . { Oxygen ——— Water
Calcium ——— Chloride of Calcium

Or in chemical symbolic notation thus :—

$$NH_3\,HCl + CaO = NH_3 + CaCl + HO.$$

If the admixture of a slight portion of atmospheric air be of no consequence, the process of *displacement*, as it is termed, may be had recourse to. The operation of displacement is one of the most common; not, however, as applied to two gases. The act of pouring fluid into a cup or bottle is one of displacement, atmospheric air being displaced by the water or other liquid. In certain cases this operation admits of being advantageously applied to the collection of gases, as, for example, in the present instance. Ammonia, in consequence of its rapid absorption by water, does not admit of collection over that liquid, and the use of mercury is inconvenient where large volumes of gas are concerned. Taking advantage, therefore, of the fact that the specific gravity of ammonia is something more than half the specific gravity of atmospheric air, we may, by careful manipulation, displace the latter by the former, without giving rise to any considerable amount of admixture. It is evident, however, that the usual condition of transference must be reversed, the receiving jar being placed mouth downward, as indicated in the annexed cut.

The process of displacement only succeeds when the gas is of such nature as to afford physical indications of its overflow. This is eminently the case with ammonia, which not only has a powerful odour, but which gives rise to dense white fumes of sal-ammoniac, when a glass rod, previously dipped in hydrochloric acid, is brought into contact with it. So soon, therefore, as the overflow of ammonia is indicated by this test, the delivery tube is to be withdrawn, and the mouth of the bottle occluded with an accurately-fitting greased glass valve.



Properties—Ammonia, as we have just recognized, is an invisible gas, having a well known pungent odour. Its density is 0·597 (by actual weighing). Ammonia is a powerful alkali; and being the first alkali that we have occasion to notice, this will be the fitting opportunity for describing the properties of an alkali generally. The most generic property of an alkali—the property common to all—is that of restoring litmus-paper reddened by an acid to its original blue, and of changing to brown a slip of yellow turmeric paper. If a slip of either of these papers acquire its original colour by the application of heat, the alkali which effected the change must have been volatile, and, for all practical purposes, it may be considered *ammonia;* nevertheless, ammonia is not, as was once imagined, the only volatile alkali: conia, the active principle of hemlock, is

another; and others, though very rare, are known to the organic chemist. With respect to the reddened litmus-paper, its preparation is a matter of some delicacy. The slip should not be reddened by immersion in an acid, however weak the latter may be. It should be held for a few instants over a portion of some volatile acid, hydrochloric acid being probably better adapted to this end than any other. Ammonia, like all other alkalies, is a powerful *base*, a term which we have scarcely had occasion to use hitherto, and which requires, therefore, a few words of comment. If we could annihilate the chemical discoveries and doctrines of the last five-and-thirty or forty years, and revive the theoretic views of Lavoisier in all their pride, their simplicity, and their fallacy, we might discuss the word base in a very summary manner, simply defining it as *that which by union with an acid forms a salt.* This statement by no means satisfies the requisitions of modern chemical knowledge; yet, despite its partial inaccuracy, it is one to which even the educated chemist clings with pertinacity, and it is one, therefore, which the young chemist may provisionally adopt, until starting from the contemplation of hydrochloric and the other hydracids, he finds the summary definitions of Lavoisierian celebrity to be inapplicable. For the present, the learner cannot do better than to assume that a base in chemical language is that which by union with an acid forms a salt. Thus, sulphuric acid, combined with ammonia as base, forms sulph*ate* of ammonia, sulphur*ous* acid sulph*ite* of ammonia, hydrochlo*ric* acid hydrochlo*rate* of ammonia, and so forth.

Ammonia is absorbed by water completely, and with extreme rapidity; hence the impossibility of collecting it over a water pneumatic trough. This property also will enable the operator to determine whether his process of collection by displacement has been successfully performed. If the receiving bottle, when immersed mouth-downwards in water and agitated, speedily fill with water, the original gas was not mixed with atmospheric air; if, on the contrary, a certain volume remains, this is a sign that the collected gas was not pure.

A jet of ammonia is not capable of burning in atmospheric air; but when injected into oxygen gas, and ignited, it burns with a pale yellow flame.

Analysis of Ammonia.—By transmitting ammonia through a porcelain tube heated to redness, partial decomposition ensues; and by repeating the operation a sufficient number of times, complete decomposition may be effected. The presence of a few clippings of platinum or copper in the tube materially facilitates the change. The metals themselves are not affected, and merely promote the decomposition of ammonia by what is termed catalysis.* The complete decomposition of ammonia is effected by transmitting it over quicklime in a tube heated below redness. If the degree of heat be more considerable, complete decomposition does not ensue. Ammonia is also decomposed by transmitting through it a series of electric sparks. If the operation be conducted in a graduated tube, the gas will be seen to continue expanding a little for each successive electric spark, until it at last occupies double the space of the original ammonia. The gas thus produced will, on examination, be found a mixture of hydrogen and nitrogen, in the ratio of three hydrogen to one nitrogen by volume. Now, a volume of hydrogen and of nitrogen correspond with an atom of each, whence the deduction is arrived at that ammonia must be a compound of three atoms or equivalents of hydrogen and one of nitrogen. Lastly, the atomic volume of ammonia may be deduced from the following consideration:—The operation of transmitting electric sparks doubled the volume of gaseous matter: hence, calling the final result four

* See page 283.

volumes, the ammonia originally present must have occupied two, and the atomic or combining volume of ammonia will be thus indicated—

Ammonia at 50° Fah. liquifies under a pressure of six and a half atmospheres; and at the very low temperature of — 113° Fah. the liquid solidifies.

Aqueous Solution of Ammonia: Hartshorn.—Under the designations, liquid ammonia, liquor ammoniæ, and hartshorn, a highly pungent fluid is sold. It is not liquid ammonia, however, but a solution of ammoniacal gas in water. This compound may be prepared either by transmitting gaseous ammonia through a series of Woulfes bottles containing water, or by distilling a mixture of sal-ammoniac lime and water, instead of the two former dry. Water can dissolve nearly half its weight, or 670 times its volume, of ammoniacal gas.

Formation of Ammonia.—Although a compound of hydrogen and nitrogen in known proportions, ammonia cannot be formed by the direct admixture of these elements. If, however, a series of electric sparks be transmitted through a gaseous mixture of hydrogen and nitrogen, small quantities of ammonia are formed; if an alkaline base be present the formation of ammonia by this treatment proceeds the more rapidly. This method of procuring ammonia, though totally unimportant as a means of producing the gas artificially, possesses great interest for the light it throws upon the source of ammonia naturally existing in the atmosphere, and which is so necessary to the existence of many growing vegetables.

In addition to the generation of ammonia by electric sparks transmitted through hydrogen and nitrogen, there are several cases in which small quantities of ammonia result from the mutual reaction of hydrogen and nitrogen whilst yet in the *nascent* state. By the expression nascent is meant to be indicated the moment at which any particular element or substance is generated or developed. Take, for instance, the case of water: if we bring the acting terminals of a voltaic combination into a vessel containing it, the water is decomposed into the two elements, oxygen and hydrogen. Whilst combined and forming water, the oxygen and hydrogen were in the condition of liquidity: when separated, they both exist in the condition of gas; and there clearly must be an instant of time at which the liquid oxygen and hydrogen cease to be liquid, and assume the gaseous form: this is said to be the nascent period.

Chemists are aware of many instances of combination between different bodies at this nascent period, which cannot otherwise be made to unite, or which unite with less facility. Hydrogen and nitrogen are in this category. When mixed together in their gaseous state, their union is accomplished with difficulty by the passage of successive electric sparks; but if brought into contact when both are nascent, the formation of ammonia takes place spontaneously. Thus, for instance, a considerable amount of ammonia is generated by acting upon metallic zinc with nitric acid, moderately diluted. The explanation is as follows:—No metal can be dissolved in an acid until the metal is oxidized: hence, when zinc is added to aquafortis, with the object of dissolving the zinc, the latter must acquire oxygen from some source before the acid can dissolve it. The source will depend upon the condition of dilution of the aquafortis: if very dilute, the zinc supplies itself with oxygen from the diluting water—hydrogen, of course, being liberated. The operation, in point of fact, is the precise counterpart of the production of hydrogen by the action of dilute sulphuric acid on zinc, and which has been explained at page 289. If the aquafortis be concentrated, the zinc is equally oxidized and dissolved; but the oxygen in this case results from a portion of nitric acid

decomposed, binoxide of nitrogen being liberated. It is possible, however, to employ aquafortis diluted to such extent that a portion of its nitric acid and a portion of its water shall be simultaneously decomposed. Under these circumstances, binoxide of nitrogen and hydrogen, exercising mutual action whilst yet in a nascent state, generate ammonia; which, combining with a portion of nitric acid yet undecomposed, gives rise to nitrate of ammonia.

We are apt to regard these productions of small quantities of ammonia as devoid of any practical interest, so far as the development of ammonia in large quantities is concerned; but by far more correct is it to remember that the production of ammonia by the combination of nascent elements is the grandest of all sources—the only one, indeed, which has any practical value—the only one which the manufacturing chemist adopts in procuring his store of ammonia.

This statement may well seem contradictory. A few pages back I have described a process for obtaining ammonia which seems to have no affinity with the combination of nascent elements. It is an ordinary case of double decomposition, resulting in the formation of chloride of calcium, and the expulsion of ammonia; hydrochlorate of ammonia and quicklime being the original substances, mixed together. But the question is, how was the hydrochlorate of ammonia originally obtained? We shall find it to have been obtained from a source involving the formation of ammonia, by the combination of nascent elements. The two chief sources of ammonia in commerce, if not indeed the only ones, are from the destructive distillation of animal matters, and from the destructive distillation of coal.

If a strip of feather, parchment, bone, flesh, silk, or almost any animal substance, except fat, be placed in a test tube, and heat applied, ammonia will be generated as one of the results. As the smell of these animal products under the influence of heat is exceedingly disagreeable, perhaps the specific odour of ammonia may not be recognizable; but its existence may be readily demonstrated by means of appropriate tests. A strip of turmeric, or reddened litmus-paper, will be affected with the peculiar signs of alkaline presence, and the discoloration, instead of being permanent, will be readily dissipated by heat; consequently the alkali must be volatile, and may be considered as ammonia. Again, a rod of glass, previously moistened with hydrochloric acid, will afford dense white fumes of hydrochlorate of ammonia, if held near the mouth of the test tube in which the destructive distillation is effected. Before the prevalence of gas illumination, all the ammonia which found its way into commerce was produced from the condensed liquor of animal matters subjected to destructive distillation. The liquor in question was technically known as *bone spirit*. It contains ammonia chiefly in the state of carbonate, mixed with numerous impurities. From these it was separated by appropriate treatment, which belongs rather to the department of applied chemistry, than to the scope of the present treatise.

A consideration of the process of making ammonia by the distillation of animal products, throws some light upon the origin of the word *hartshorn*. If hartshorn shavings be subjected to destructive distillation, they will evidently yield ammonia. In this respect they are neither better nor worse than thousands of other animal bodies; but the horn of deer acquired a celebrity as an ammoniacal source at a very early period of chemical history—wherefore, it is not easy to say. By far the most considerable source of ammonia at present is a liquor which condenses in gas mains, and which, in addition to ammonia, contains a multiplicity of other substances. The immediate point for our consideration is this:—the whole of the ammonia found in

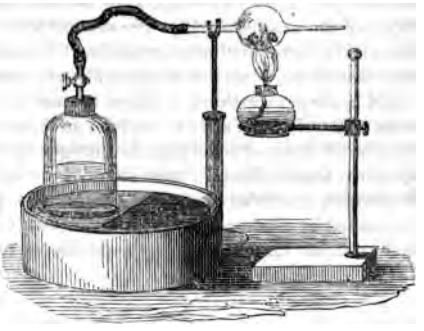
these products has been generated by the contact of hydrogen with nitrogen during the process of destructive distillation.

Remembering the composition of ammonia, the result of union between hydrogen and nitrogen, it will be evident that this material is only susceptible of being yielded by nitrogenous substances. Hence it is that animal bodies, owing to their richness in nitrogen, yield far more ammonia than vegetable substances—at one time, indeed, it was customary to speak of vegetable bodies as being totally deficient of nitrogen. This, I need scarcely remark, was a fallacy; but the implicit beliefs of a past age are seldom devoid of some foundation, and may continue to be accepted as broad marks of distinction between species long after the belief in the universality of the distinction has passed away. As a general rule, animal bodies contain nitrogen, and vegetable bodies do not; yet enormous quantities of nitrogen are locked up in the vegetable kingdom. Pit coal, indeed, is a vegetable production; and from pit coal do we now obtain the largest quantity of our ammonia. In the vegetable kingdom certain natural families are remarkable for the large quantities of ammonia which they contain. The natural families *Cruciferæ*, *Fungaceæ*, and *Solanaceæ*, may be cited as instances; and every person is aware of the disagreeable quasi-animalized odour yielded by the decomposition of these. The disagreeable smell of water in which cabbages have been boiled is proverbial; and cabbages belong to the natural order *Cruciferæ*, or *Brassicaceæ*. Again, mushrooms (*Fungaceæ*) so nearly approach the characteristics of animal bodies, that when undergoing decomposition, even flies are deceived, and select them as foci for the deposition of eggs. Any tobacco smoker may readily convince himself of the presence of ammonia in the smoke of his favourite herb. He has only to hold a strip of test-paper in the smoke, and the demonstration is more than half made. He may complete the demonstration by substituting for test-paper a glass rod dipped in hydrochloric acid; or still more affirmatively by passing tobacco smoke, by means of a glass tube, into a dilute acid, when the peculiar ammoniacal combination of that acid will be formed in considerable quantities.

Connected with the spontaneous formation of ammonia, there is a remarkable circumstance which has already been indicated,—the presence of nitrate of ammonia in rain-water. The sources, both of this ammonia and its associated nitric acid, may be referred to electric and atmospheric agencies; though doubtless these constitute but a fraction of the causes in operation. Notwithstanding the diametrically opposed chemical natures of ammonia and nitric acid, there is reason to believe that in certain natural operations the latter may be instrumental in generating the former. There is a beautiful experiment which illustrates so remarkably this point, that I shall describe it. The experiment is as follows:—First take a few shreds of asbestos, saturate them with solution of chloride of platinum, dry them, and ignite to redness. By this operation the chloride of platinum will be decomposed, leaving a film of metallic platinum in the minute interstices of the asbestos. The function of this platinized asbestos is similar to that of spongy platinum and platinum black, already mentioned (p. 294). Next prepare an apparatus of the following description:—

A gas jar is supplied with a stopcock, and a flexible tube in connection, by its other extremity, with a glass tube, blown into a bulb towards the middle, and terminating in a jet at its furthest extremity. Into the jar is transmitted a gaseous mixture of two volumes binoxide of nitrogen, and five volumes hydrogen: into the bulb is placed the platinized asbestos just described. As the pneumatic trough contains water, it follows that by depressing the jar, a flow of mixed gas will be determined along the tube and over

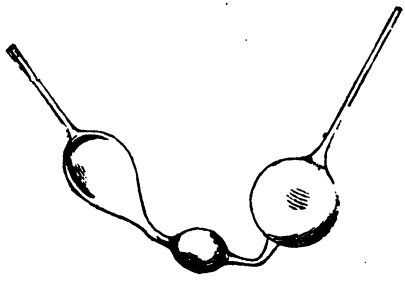
the platinized asbestos. If this be done without the application of any heat to the bulb containing the platinized asbestos, the terminal jet will be seen to liberate copious ruddy fumes of hyponitrous, nitrous, and perhaps nitric acid. They are evident enough by mere inspection; but for the sake of more complete demonstration, they may be caused to impinge against a piece of litmus-paper, which they will immediately colour red, and thus demonstrate their acid character. But if whilst the current of gas is passing a spirit-lamp flame be held under the bulb, decomposition of the binoxide will ensue, its nitrogen uniting with hydrogen to constitute ammonia, the presence of which will be evidenced by reconverting the reddened litmus-paper to its original blue colour. There is great probability that some effect, analogous if not identical with this, takes place in certain operations of nature.



But the mutual affinities between hydrogen with oxygen, and nitrogen with oxygen, are so nicely balanced that the existence of ammonia, or of nitric acid, will be determined by very slight causes. I have shown how a mixture of binoxide of nitrogen with hydrogen can generate ammonia; the converse experiment may now be described, which is as follows:—If a mixture of sal-ammoniac and quicklime be placed in a retort, the retort connected with an iron tube containing peroxide of manganese, and heated to redness by passing through a furnace, we shall, on applying heat to the retort, and thereby forcing ammonia through the peroxide, generate fumes of hyponitrous, nitrous, and nitric acid. The theory of this result is referable to the evolution of oxygen by the binoxide of manganese, and the combination of that oxygen with the nitrogen of the ammonia.

Quantitative Estimation of Ammonia.—This may be roughly effected by causing it to unite with a base, crystallizing the resulting salt, weighing, and calculating the amount of ammonia from the datum of the known composition of the salt. Far more correct, however, is the method of throwing it down in the state of chloroplatinate of ammonia, by adding a solution of chloride of platinum to a solution of ammonia in hydrochloric acid. The chloroplatinate of ammonia thus generated is a yellow salt, not very soluble in water, but almost completely insoluble in a mixture of ether and alcohol. If, therefore, a liquid, or a gas containing ammonia, be brought into contact with hydrochloric acid, combination immediately ensues, hydrochlorate of ammonia being the result; and if the liquor containing it be evaporated almost to dryness, and a mixture of alcohol and ether added to the residue, the chloroplatinate of ammonia is rendered insoluble, and being collected on a tared filter, its weight may be estimated. Knowing this weight, the chemist, by a simple calculation, is informed concerning the amount of ammonia originally present; and not the ammonia merely, but the nitrogen constituting ammonia. Thus it will be seen the chloroplatinate of ammonia is, in point of fact, a quantitative test of the presence of nitrogen; it is, indeed, generally employed for this purpose in cases of organic analysis, as will appear in the sequel when organic analysis shall be discussed. It remains now to state that every 100 parts of the chloro-

platinate correspond with 7·692 of ammonia, and 6·334 of nitrogen. The employment of this, as well as any other re-agent for the purposes of chemical analysis, involves many precautions; these I have not here mentioned, because chemical analysis is not the object of the present work. The student will do well to reflect on the apparently tortuous and indirect method of estimating the quantities of ammonia or of nitrogen present by means of the formation of the platinum compound. He may perhaps think that it would be far more rational to collect the ammonia or the nitrogen respectively, and have them well before the senses. Not so: in the earlier days of organic chemistry, chemists were in the habit of collecting the nitrogen and estimating it in this condition; but the operation was so difficult, was attended by so many disadvantages, that so soon as Warrentrap and Will discovered the indirect process of estimation just described, it was hailed by chemists as a great boon, and on all practicable occasions adopted. I shall conclude these remarks by appending a representation of the apparatus in which the absorption of ammonia by hydrochloric acid is usually adopted, anterior to its precipitation by chloride of platinum. A glance at the construction of the instrument will demonstrate its applicability to this purpose. Consisting of three bulbed expansions as it does, the gas, during its transmission, is certain to be brought well into contact with the hydrochloric acid, the chief object held in view; and when the absorption is complete, the fluid may be readily transferred to any convenient vessel in which to effect the precipitation.



Imidogen, Amidogen, and Ammonium.—We are acquainted with neither of these bodies in a separate state—their existence is altogether hypothetical; there are good reasons, however, for assuming the existence of the two latter, at least.

Amidogen.—If potassium or sodiun be heated in ammoniacal gas, a solid compound is formed; this compound, however, is not one of ammonia and potassium, or sodium, for during the combination one-third of the hydrogen existing in ammonia escapes. It must, therefore, be composed of K or N (the symbols for potassium and sodium), united with NH_2; and to this hypothetical body NH_2, the designation of amidogen has been applied. The preceding is only one of several cases involving the production of amidogen, and the formation of compounds termed amides.

Ammonium.—Although this body has never been isolated, the arguments in favour of its existence are very strong. Ammonium is a compound of hydrogen and nitrogen, as we have seen; but its name should be indicative of a metallic character, if the analogies of ordinary nomenclature are to be respected; and, indeed, ammonium acts so like a metal that, notwithstanding its compound character, we can hardly refuse to consider it as such. The most direct evidence in favour of the existence of ammonium is that of the ammonium amalgam, as it is called. The easiest method of forming the ammonium amalgam is the following:—Alloy mercury, with one per cent. of sodium; pour the alloy into a cold saturated solution of sal-ammoniac,—hydrochlorate of ammonia, as we have already called it, but which shall now be denominated by its more modern name, chloride of ammonium. The alloy thus treated prodigiously

expands, sometimes as much as two hundred times its original size, still retaining its solidity, and acquiring the consistence of butter. Meantime its metallic lustre is not in the least impaired, and it augments in weight. If we grant that the mercury has combined with a metal, and formed an amalgam, the explanation is easy; but granting this, we must assume the existence of a metal composed of NH_4, a somewhat startling assumption, seeing that ever since the days of alchemy metals have been set down as simple undecomposable bodies.

Whether the hypothetical compound ammonium—metal or no metal—can exist except in combination, is unknown. Hitherto chemists have failed to accomplish its isolation. Its theoretical existence, however, is fully admitted; and chemists speak of chloride of ammonium with the same confidence as when speaking of chloride of potassium or sodium.

SULPHUR.

Atomic weight	16
Atomic volume $\frac{1}{8}$th at	900°
Atomic volume $\frac{1}{2}$ or ▭ at	1800°
Specific gravity of solid	1·98
Do. of vapour (at 900°)	6634
Do. (at 1800°)	2214

General Notice.—The natural history of the element under consideration differs from the natural history of those already mentioned in one important particular. It is found in nature uncombined, or *native;* large depositions of sulphur, almost pure, occurring in Sicily and other volcanic regions. A far larger proportion, however, occurs in combination with metals,—constituting sulphurets, as these compounds are denominated, or perhaps more generally, in the language of modern chemistry, *sulphides*. And now, having introduced the reader to a new denomination of chemical nomenclature, we must pause for the object of explaining it, seeing that our preliminary consideration of chemical names was but slight, and that the explanation of each new name was promised to be made as the necessity for learning it should occur. The terms sulphuret and sulphide, then, are synonymous: they indicate a direct combination of sulphur with a second body; thus, a combination of sulphur and lead forms the sulphuret or sulphide of lead: of iron, the sulphuret or sulphide of iron, and so forth. Frequently it is desirable that the name should indicate the exact relation subsisting between the sulphur and second body, in any given sulphuret; this is done by enlisting into our service the prefixes, *proto*, *sesqui*, *bi*, *per*, &c., giving rise to the terms protosulphuret, sesquisulphuret, and bisulphuret. If the term sulph*ide* occur, the student should be careful in discriminating between it and the term sulph*ite*. The former indicates a binary compound of sulphur with a second body; whereas the latter designates the salt resulting from the combination of sulphur*ous* acid with a base.

To resume our sketch of the natural history of sulphur, not only does it exist native, and as a constituent of numerous minerals, but it enters into the composition of many vegetables, and perhaps all animal tissues and animal fluids. The onion or lily tribe is remarkable for the amount of sulphur which its members contain; so is the natural order *Brassicaceæ*. Most persons will have remarked how speedily a silver spoon blackens if immersed in the mustard-pot: this blackness is indicative of the presence of sulphur. With still greater rapidity does a silver spoon blacken if plunged into a boiled egg, proving the existence of sulphur there. Silver

and its compounds, indeed, are good tests of the presence of sulphur; but lead and its combinations are still better. A solution of oxide of lead in caustic potash and water (liquor potassæ of pharmacists) is the most delicate test we possess for the indication of sulphur in organic bodies. If a bit of feather, or wool, or silk, or indeed almost any animal body, however old and worn, be brought into contact with some of this potash-lead solution in a small test-tube, and heat applied, a dense blackness almost immediately occurring at once indicates the presence of sulphur.

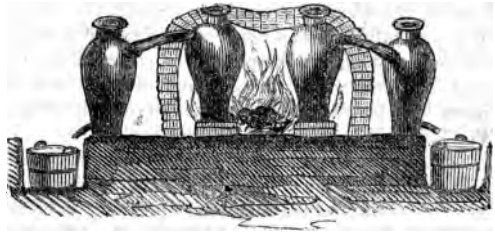
The condition of sulphur as regards aggregation differs from either of the non-metallic elements already discussed. Under ordinary circumstances of temperature and pressure it is a solid, but it readily fuses into a liquid; and if the heat be still further increased, the liquid expands into a vapour or gas—for in the strict logic of chemical science there is no specific difference between a vapour and a gas. In addition to the three physical conditions as above, this element is subject to a remarkable allotropic condition, to be described hereafter.

Sulphur frequently occurs in the condition of an amorphous mass, but it may be readily crystallized; and, according to the treatment followed, the resulting crystals may belong to one of two different crystalline systems. The prevalent form of sulphur, made to crystallize by fusion and slow cooling, is an oblique prism, with rhombic base —a form characterizing the oblique prismatic system; but if sulphur be dissolved in liquid sulphuret of carbon, and the solution cautiously evaporated, regular octohedral crystals are produced with rhombic bases, these being characteristic of the right square prismatic system.

Allotropic condition of Sulphur.—When describing oxygen at page 286, I mentioned the circumstance of its assuming a second condition, to which the term ozone had been applied. Sulphur is similarly circumstanced: it is prone to assume a second or allotropic condition. If common yellow sulphur be heated in a Florence flask it speedily melts, becoming converted into a transparent straw-coloured liquid. Still increasing the heat, a curious phenomenon is observable: the transparent, liquid, almost colourless fluid, thickens to the consistency of treacle, the dark colour of which it also assumes; it then solidifies so completely that the flask may be inverted without spilling its contents. Still increasing the temperature, the darkened sulphur fuses once more; but the fused result does not lose its dark colour. The physical distinction between ordinary yellow sulphur and the same element in its second or allotropic state is best recognized by pouring some in each condition of fusion into cold water. The colourless fluid yields ordinary yellow sulphur, but the coloured treacly mass chills into a material possessing very much the aspect of india-rubber: it is allotropic sulphur. The tenacious mass thus resulting is an excellent material for taking impressions from coins or other raised surfaces, and had long been used for that purpose before the doctrine of allotropism had been studied. This doctrine is altogether recent; and the phenomena which it investigates are recognizable in various substances, both simple and compound. As to the *rationale* of these second conditions of existence, nothing satisfactory is known; and in certain cases theory even is unable to assume a plausible explanation. Had the chemist merely to deal with allotropic conditions of compound bodies, theory would come to his aid: he might assume the existence of a fresh arrangement of particles; but in cases where only one kind of particles is involved, as in the instances of sulphur and of phosphorus, there is clearly no scope for assumptions of this kind. Not only is the physical appearance of allotropic sulphur different from those of the ordinary material, but its chemical relations are in some degree also different. For example:

its fusing point is different, as we have seen; and it ceases to be soluble in bisulphuret of carbon, whereas ordinary sulphur is very soluble in that liquid.

Fused sulphur is vapourized at temperatures of about 550° or 600° Fah., and may then be readily distilled. This treatment is adopted in order to obtain the material pure, on the large scale. The native sulphur of Sicily, and other volcanic regions, is largely contaminated with non-volatile earthy bodies, and a large amount of volatile impurities. The first rough process of purification consists in exposing the sulphureous materials to a temperature above the fusing point of sulphur. The latter melts and collects on the surface of the mass, whilst the earthy bodies sink below. The fused sulphur, brought to this condition, is poured off and allowed to consolidate. It is still far from pure, and is known in commerce under the name of sulphur *vivum*. The next stage in the purifying operation is a rough distillatory process, conducted by means of earthenware pots arranged in pairs—one serving as retort or distillatory vessel, the other as receiver. The retort pot is completely enveloped by an oven, with the exception of the neck or beak, which passes through, and communicates with the receiving-pot outside. In this vessel a considerable amount of sulphur is condensed; but a still larger portion is conveyed into a vessel full of cold water. The accompanying diagram illustrates this arrangement.



Sulphur thus resulting is still very impure, containing from 10 to 15 per cent. of impurities. To effect separation of the latter, a second, and more perfect, distillatory process is required. The apparatus employed for this purpose is a large retort of brickwork, the beak of which is very capacious, and terminates in a vaulted brick chamber. By means of this apparatus, the purified sulphur may be obtained in masses or in powder, at the operator's will. Powdered sulphur is known in commerce as flowers of sulphur; and the solid mass, after having been fused and cast into cylindrical moulds, constitutes the stick sulphur or brimstone. Flowers of sulphur is not usually so pure a material as solid stick brimstone, the former being usually contaminated with sulphurous acid, which can only be separated by washing. Sulphur is an important element of several manufacturing processes, amongst which those of gunpowder and oil of vitriol merit especial notice.

Combinations of Sulphur with Oxygen.—A list of these compounds has already been given at page 285, but it will be proper to repeat it in this place.

1.	Hyposulphurous acid	$S_2\ O_2$
2.	Trisulphuretted hyposulphuric acid (*Pentathionic acid*) .	$S_5\ O_5$
3.	Bisulphuretted hyposulphuric acid (*Tetrathionic acid*) .	$S_4\ O_5$
4.	Sulphuretted hyposulphuric acid (*Trithionic acid*) .	$S_3\ O_5$
5.	Sulphurous acid	$S\ O_2$
6.	Hyposulphuric acid (*Dithionic acid*) . . .	$S_2\ O_5$
7.	Sulphuric acid	$S\ O_3$

It is not desirable to treat of these combinations in the tabular order of their occurrence. Sulphurous acid is the starting point of all the combinations of sulphur with oxygen. To sulphurous acid, therefore, our first remarks shall be directed.

SULPHUROUS ACID.

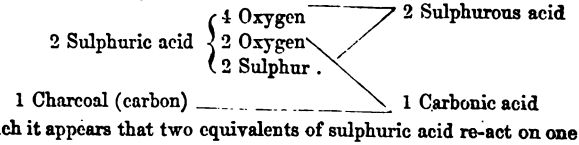
Atomic weight	32.
Atomic or combining volume	[ ] .
Specific gravity	2247.

General remarks.—It is not easy to say to whom the first chemical apprecia sulphurous acid is referable; the antiquity of its manufacture, however, must be coeval with the first knowledge of sulphur, inasmuch as this body when bu atmospheric air generates sulphurous acid.

Preparation.—(1). By the combustion of sulphur in atmospheric air.—T ready means of generating sulphurous acid has just been indicated—namely, tl bustion of sulphur in atmospheric air, with the oxygen of which it combines. however, sulphurous acid cannot be obtained pure by this process; the nitro carbonic acid of the atmosphere must occur in admixture with it. Practicall ever, the presence of nitrogen and carbonic acid are of no importance in operations, involving the employment of sulphurous acid. A very important this kind will be mentioned in the sequel.

(2). By the combustion of sulphur in oxygen gas.—This operation yields sul acid in the condition of purity. It is never adopted, however, in practice, bein less convenient method than others presently to be described.

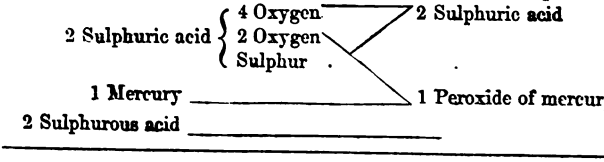
(3). By heating oil of vitriol, hydrated sulphuric acid, in contact with some dizing body.—Charcoal answers very well for this purpose, provided the simul presence of carbonic acid, which is also generated, be of no consequence. The tion may be conducted in a Florence flask, to which a perforated cork and be have been attached. The source of heat may be a spirit-lamp flame, and the re gas should be washed by transmission through a bottle containing a little wate charcoal employed should neither be in mass nor finely pulverulent. If the the action is sluggish; if the latter, it is too violent. The charcoal should be by hammering, and all the powder, as well as large pieces, rejected. The am oil of vitriol should be a little more than the quantity required for completely the charcoal. The decomposition which ensues is illustrated by the following di



From which it appears that two equivalents of sulphuric acid re-act on one of cl yielding two equivalents of sulphurous acid, and one equivalent of carbonic aci

If circumstances require that the sulphurous acid be liberated unmixed other bodies, we must substitute one of several metals capable of decomposi phuric acid. Copper may be employed for this purpose, but mercury is still bet

The annexed diagram illustrates the nature of the decomposition.



(4). By heating in a retort or flask a mixture of six parts peroxide (binoxide or black oxide) of manganese, with one part of powdered sulphur.—The resulting sulphurous acid requires to be washed by transmission through a bottle containing a little water, in order to separate a portion of volatilized sulphur which passes over.

The student will readily anticipate the nature of this decomposition. Already (page 282) we have seen that peroxide of manganese yields oxygen when heated; it is accordant with our preconceptions, therefore, that sulphur, greedy as it is of oxygen, should absorb a portion whilst yet in a nascent state, and become converted into sulphurous acid; such, indeed, is the decomposition which really takes place.

General Properties.—Sulphurous acid usually assumes the condition of a gas. In this state we have already assumed it to be procured; but it is readily condensed into a fluid, and by the operation of extreme cold and pressure it may be solidified. It may be condensed into a fluid by the operation of cold alone; a temperature of 14° Fah. sufficing for this purpose. Under a pressure of two atmospheres sulphurous acid may be liquified at a temperature of 57° Fah. Liquid sulphurous acid is a colourless, very mobile fluid, having a specific gravity of 1·42. It evaporates with great rapidity, producing extreme cold, as low as 43°, or 46°, according to the temperature of the surrounding air. Sulphurous acid gas is colourless, pungent, neither combustible nor a supporter of combustion in the common acceptation of these terms—it is soluble in water, to which it imparts its peculiar taste and smell—it combines with bases, forming the class of salts termed sulph*ites*, which effervesce when acted upon by a stronger acid, sulphurous acid being liberated. It combines with several colouring matters, with which it forms colourless compounds; it is, therefore, a bleaching agent, and is applied, with this object in view, in many branches of manufacture—for example, ladies' straw bonnets are whitened by enveloping them in an atmosphere of sulphurous acid, and sponges are bleached by keeping them some time immersed in an aqueous solution of this acid. A very elegant experiment illustrative of the bleaching effect of sulphurous acid, consists in moistening a red rose, and holding an ignited brimstone match underneath the red petals—they are almost immediately turned white by this treatment. But the whiteness is not permanent: the original colour will reappear on dipping the rose into a solution of almost any stronger acid; for this purpose dilute sulphuric acid answers very well.

If sulphurous acid be brought into contact with acetate of lead in solution, a copious deposition of white sulphite of oxide of lead (commonly termed sulphite of lead) takes place, until all the lead is separated, and acetic acid, holding sulphurous acid in solution, remains. From a solution of this kind, however, all the sulphurous acid may be dispelled by allowing it to stand exposed to the air in a shallow pan for some days. Sulphurous acid, in point of fact, is perhaps the most complete separator of lead from the acetate of that metal with which chemists are acquainted, as I pointed out some years since—far more complete than sulphuric acid; and if not more complete than hydrosulphuric acid, having unquestionably a peculiar sphere of applicability. For example, sulphurous acid may be employed to throw down lead out of a sugar solution without injuring the sugar, although sulphuric and hydrosulphuric acid would destroy it completely. Taking advantage of this fact, I devised a scheme of sugar manufacture in the year 1847, which has since been extensively applied.

If an aqueous solution of sulphurous acid be kept for a considerable period, and more especially if retained in a warm situation, small quantities of sulphuric acid will be generated. This is an important fact—it is referable to the tendency possessed by

sulphurous acid to combine with oxygen. This tendency, in point of fact, is the strongest characteristic associated with sulphurous acid in the chemical mind, and determines some of its most interesting effects. A treatise on chemistry is necessarily filled with numerous matters possessing various degrees of relative importance. Some are the very keys of the science, by the application of which its stores of knowledge are unlocked; others are of less importance, and need not occupy the mind of a general student. The successful study of chemistry will greatly depend on a just discrimination between facts of major and of minor importance. The student should be taught to seize the broad characteristics—the *physiognomy* (if the expression be allowable) of the objects brought under his notice. Of this kind is the fact that sulphurous acid possesses a strong tendency to unite with oxygen, and is frequently employed as a deoxidizing agent by the chemist.

Although sulphurous acid by prolonged contact with water can generate sulphuric acid, the operation is far too slow to admit of any large practical application; but if we proceed in the line of experiment, which the solution of sulphurous acid in water suggests to us, we shall soon arrive at the commercial process of manufacturing oil of vitriol. If sulphurous acid be able to remove oxygen from water, theory suggests that it should be able to remove it still more easily from bodies still more rich in oxygen. Nitric acid, or, more properly speaking, aquafortis (hydrate of nitric acid) is of this kind. Nitric acid contains, as we have already seen, five atoms of oxygen (page 314); and here it may be desirable to mention, that nitric acid, in relation to oxygen, is the very reverse of sulphurous acid, the latter being a powerful deoxidizing agent, the former ever ready to give up a portion of its oxygen.

If, therefore, a current of sulphurous acid be transmitted through hot nitric acid, decomposition of the latter ensues; fumes of hyponitrous and nitrous acid are evolved, thus proving that the nitric acid is suffering decomposition. If hyponitrous and nitrous acid fumes are evolved, it follows that a portion of oxygen must have been removed; and, after the remarks just made concerning the avidity for oxygen manifested by sulphurous acid, it will readily be inferred that the missing oxygen must have been laid hold by sulphurous acid, and sulphuric acid generated. So strong is the tendency of nitric acid to give off oxygen when brought into contact with a body having a strong affinity for that element, that pure sulphur can be converted into sulphuric acid by prolonged boiling in nitric acid. Chemical analysts, indeed, employ this very process for the purpose of estimating the amount of sulphur contained in certain bodies. Instead of getting out the sulphur bodily under its own proper aspect, they oxidize it by means of nitric acid, convert it into sulphuric acid, and from the amount of sulphuric acid generated calculate the original amount of sulphur.

Determination of the Composition of Sulphurous Acid.—This may be readily accomplished by a synthetical operation, as follows:—Fill the globular portion of a glass flask with oxygen gas, and dip the neck of the flask in mercury, taking care that a portion of mercury rise up into the neck. Now, having attached a small piece of sulphur to the end of a wire, plunge the sulphur up through the mercury into the body of the glass flask. By means of a burning lens, the sulphur is now to be ignited. It will continue to burn, combining with oxygen and yielding sulphurous acid, as we have already seen (page 284);

but the volume of the original gas will not have been altered, from which circumstance we infer that sulphurous acid gas must contain its own volume of oxygen, united with sulphur. How much sulphur? is the next question to be determined. We can arrive at this solution in the following manner:—

Density or specific gravity of sulphurous acid gas, represented by the weight of one volume	2·247
Do. of oxygen represented by one volume	1·106
One-sixth (nearly) of the density or specific gravity of the vapour of sulphur, thus corresponding with one atom (see page 335)	1·141

Sulphurous acid is therefore, according to this synthetical demonstration, a compound of one-sixth volume of sulphur (one atom), in combination with one volume, or two atoms, of oxygen, and is, consequently, thus indicated by chemical symbols,—

$$SO_2.$$

SULPHURIC ACID.

Atomic weight 40

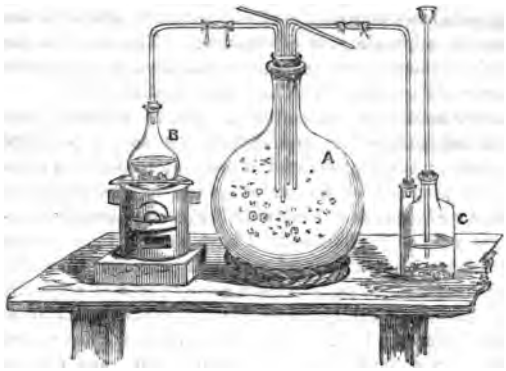
General Properties.—Sulphuric acid in its uncombined condition is a very rare substance, having somewhat the appearance of snow. It can only exist whilst sealed in vessels from which all moisture, atmospheric or otherwise, is excluded; for its tendency to unite with water is great. It combines with water in several proportions, two of which are well known—namely, the acid of Nordhausen (so called from the place of its manufacture), composed of two equivalents of real sulphuric acid with one of water, and the monohydrate of sulphuric acid of commerce. The latter is the strongest oil of vitriol of English commerce, and, as its name indicates, is a compound of one equivalent of real sulphuric acid combined with one equivalent of water.

Preparation.—The most direct method of preparing anhydrous sulphuric acid consists in passing a mixture of sulphurous acid and oxygen over spongy platinum contained in a tube heated to redness; but the operation is only interesting in a theoretical point of view. It may be prepared in greater quantities by distilling fused bisulphate of soda; but the most ready means of obtaining it in a considerable quantity is by distilling the sulphuric acid of Nordhausen. I have already indicated the composition of the latter, as a compound of two of real acid plus one of water. Perhaps, however, it is more philosophical to regard it as a solution of real sulphuric acid in the monohydrate of the same, for a great difference exists as to the readiness with which its two parts of real acid are evolved. If the Nordhausen acid be exposed to distillation, an equivalent of its real acid is given off with facility, and may be collected in a proper recipient; but the second equivalent retains its amount of water with such obstinacy that both may be distilled over unchanged if the temperature be sufficiently elevated.

Nordhausen, or fuming Saxon Sulphuric Acid.—The nature and composition of this substance having been indicated, it now remains to describe its mode of preparation, which is as follows:—Protosulphate of iron (green vitriol or copperas), a salt composed of one atom of sulphuric acid, one of protoxide of iron, and seven of water,—consequently, of which the formula is $Fe\,O.\,SO_3 + 7HO$—is exposed to the action of heat in open vessels, by which means six equivalents, or atoms, are liberated; but the

seventh, maintaining its union with greater obstinacy, remains. By still increasing the degree of heat, a portion of sulphuric acid is decomposed, yielding oxygen to the protoxide of iron, which it converts into sesquioxide, Fe_2O_3, and which, in its turn, unites with the remaining sulphuric acid. Still increasing the heat, the sulphate of sesquioxide of iron is decomposed, its sulphuric acid being evolved in combination with water, and peroxide of iron remaining. Such is the preparation of the Nordhausen sulphuric acid; it is a compound far inferior both in utility and interest to the monohydrate of sulphuric acid, presently to be described.

Monohydrate of Sulphuric Acid (*Oil of Vitriol*).—The most advantageous point from which to commence our study of oil of vitriol, as commercially produced, will be that portion of our remarks which relate to binoxide of nitrogen, and the higher oxygen compounds which it is capable of forming, up to the maximum, which is nitric acid. It will be remembered (p. 323) that binoxide of nitrogen is itself a colourless gas, which immediately gives rise to ruddy fumes when allowed to come into contact with atmospheric air, or any gas containing oxygen. It will be remembered, moreover, that these ruddy fumes are a mixture of the higher oxygen compounds of nitrogen with each other; are a mixture, therefore, of hyponitrous, nitrous, hyponitric, and nitric acids. Now we have seen (p. 340) that sulphurous acid can decompose nitric with the generation of sulphuric acid; but the circumstance still remains to be indicated, that nitric acid is not peculiar in this respect. Nitrous acid can be decomposed by sulphurous acid—so can hyponitrous acid, and even, under some conditions, binoxide and protoxide of nitrogen. This point being well remembered, the process of the oil of vitriol manufacture will be readily apprehended. I will now proceed to illustrate the changes which ensue, by means of a simple experiment:—A is a glass flask slightly moistened with water, and furnished with a cork having four perforations, two of which are in tubular communication with flasks, and two open freely into the air; the latter are for the object of preventing the rupture of the large flask by the sudden pressure of gas within. The flask C contains a mixture of copper and diluted nitric acid, and of course will liberate binoxide of nitrogen. The flask B contains mercury and oil of vitriol, and consequently, when heat is applied, will liberate sulphurous acid. If, then, by means of this arrangement sulphurous acid and binoxide of nitrogen be brought into contact with aqueous vapour in the large flask, certain phenomena will be observed illustrative of the manufacture of oil of vitriol. The first phenomenon to be observed is the conversion of binoxide of nitrogen into ruddy fumes of hyponitrous and nitrous acids; the second is the generation of small acicular crystals; the third, the total disappearance of these crystals if the cork be removed and water poured in; the fourth, the existence of oil of vitriol in the resulting solution; the fifth,



the liberation of binoxide of nitrogen during this act of solution. Binoxide of nitrogen may easily be recognized by the generation of ruddy fumes.

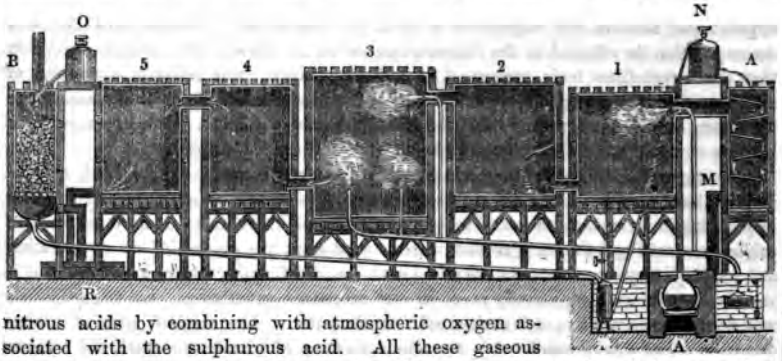
Supposing these various stages to have been gone through, it is evident that after having generated a certain amount of dilute oil of vitriol, we shall have arrived at the point from which we started, that is to say, we shall have reproduced a mixture of hyponitrous, nitrous, and sulphurous acids in the large globe. Precisely this scheme of decomposition is effected in the manufacture of oil of vitriol, with the sole exception that the crystalline body generated in our experiment—and being a compound of nitrous and sulphurous acids—is avoided by the manufacturer; its existence shows the deficiency of aqueous vapour, and he hastens to supply more. We are now in a position to understand the nature of the oil of vitriol manufacture.

The apparatus for conducting this manufacture, though variously modified, may be divided into two portions; the first consisting of a series of leaden chambers corresponding in formation to our large glass globe, and serving to retain a mixture of sulphurous acid and the oxygenated nitrous products; the second of an evaporating and a distillatory apparatus for depriving the acid of much water, with which it is combined; for we have already seen, in our miniature experiment, that the sulphuric acid resulting occurs in combination with much water. The original plan of manufacturing oil of vitriol consisted in burning a mixture of nitrate of potash and sulphur in a close furnace, and conveying the results of combustion into a series of leaden chambers covered a few inches deep with water. Those results are a mixture of sulphurous acid with binoxide of nitrogen, the latter changing to hyponitrous and nitrous acids immediately it comes in contact with the atmospheric air contained in the leaden chamber, and hyponitrous and nitrous acid reacting upon the sulphurous acid and watery vapour, causing the layer of water on the floor of the leaden chamber to be impregnated with dilute sulphuric acid, as we have already seen. It remained to convert the dilute sulphuric acid thus generated into concentrated oil of vitriol, which was accomplished by driving off the excess of water by means of heat. The heating process was, and indeed still is, commenced in leaden boilers, but it was finished in retorts of glass. Instead of glass, large retorts of platinum are at present substituted. Modifications of this process of oil of vitriol manufacture are now adopted, to the exclusion of the original. One of the most complete processes of this kind, and the apparatus employed in conducting it, I shall now proceed to describe.

It is represented by the diagram on page 344, and consists, as will be seen, of five leaden chambers, connected with each other by flues, and associated with other apparatus to be described hereafter.

Let us commence our description of this apparatus at the part marked A, which represents the ash-pit of a small grate or furnace, the fuel consumed in which is iron pyrites (sulphuret of iron). The heat evolved by this combustion serves to vapourize some water contained in a vessel represented in our diagram immediately over the furnaces, and which will be seen to communicate by means of pipes with chambers 1 and 3, also with the little vessel P. Tracing now the direction pursued by the evolved sulphurous acid gas, we perceive that it goes through the chimney M into the vessel A, where it comes into contact with a stream of oil of vitriol highly charged with nitrogenous compounds of oxygen proceeding from the leaden vessel N; the source of which will be indicated hereafter. In the vessel A are represented slanting sheets of lead; these being for the purpose of dispersing the stream of nitrogenized oil of vitriol into thin layers, and bringing it into contact with the ascending fumes of

sulphurous acid. No sooner does sulphurous acid touch the nitrogenized oil of vitriol, than mutual reaction takes place; a portion of sulphurous acid becoming sulphuric acid by abstraction of the necessary oxygen. As a result of this decomposition, binoxide of nitrogen is formed, and immediately converted into hyponitrous and



nitrous acids by combining with atmospheric oxygen associated with the sulphurous acid. All these gaseous materials now pass on into the chamber No. 1, the gaseous flow being expedited by a jet of steam, as represented in the woodcut. But the steam jet has a chemical function to perform also; it has to prevent the generation of the crystalline body described at page 342, and to determine the formation of sulphuric acid, which it does so effectually that all the oxidizing nitrogenous compounds resulting from the impregnated oil of vitriol, supplied by the vessel N, are exhausted of their disposable oxygen in the first chamber, or No. 1, so that the gaseous current which enters No. 4 is little else than sulphurous acid mingled with atmospheric air. In order that the continuous formation of sulphuric acid should go on, it is therefore necessary to supply a fresh portion of oxidizing materials. This is accomplished by the continuous dropping of portions of nitric acid upon pieces of brick, represented lying on the floor of chamber D. No aqueous vapour is conducted into this chamber, but the gases are allowed to mingle thoroughly, preparatory to their almost final exhaustion in the large chamber No. 3, where they meet with abundance of aqueous vapour, as the diagram sufficiently represents. Chambers 4 and 5 are to be regarded as little else than refrigerators, and in the vessel R the process of refrigeration is still further perfected by the agency of cold water externally applied. Nevertheless, some of the gaseous ingredients will escape—more especially a remnant of nitrogenous gases—into the cylinder B, where a special provision is made for retaining them. In B will be recognized some large pieces of coke, which are continuously moistened by a stream of oil of vitriol coming from O. By this treatment the oil of vitriol becomes charged with nitrogenous vapours, and ultimately finds its way, by a peculiar contrivance, into the vessel N, where we have already recognized its presence and intimated its function. The means by which the nitrogenized oil of vitriol is conveyed from B to N are simple enough. It necessarily flows into P by simple descent, and it is elevated from P to N by the pressure of steam, turned on when required from the steam-boiler.

Chemical Properties of Sulphuric Acid, its Method of Determination and Analysis.—Some of the properties of pure sulphuric acid have already been described. This substance is of inferior importance to the chemist, as it seldom or never occurs in the

course of analytical operations. Sulphuric acid in solution or combination are the conditions which usually present themselves to his notice. The strongest sulphuric acid of English commerce (oil of vitriol) is a compound, as I have already mentioned, of one equivalent real sulphuric acid, and one equivalent of water. It has the physical appearance of an oil, whence its name. Its specific gravity is about 1·850. It rapidly unites with water, evolving much heat in doing so. It chars organic matters when brought into contact with them, this effect being referable to its affinity for water, as the following explanation will make evident. Organic bodies, as the rule, are compounded of oxygen, hydrogen, and carbon, with or without nitrogen; hence, if oxygen and hydrogen be removed in the form of water, the carbon, either with or without nitrogen, will remain. But the natural form of carbon when isolated is a black solid (charcoal), and thus the clearing operation is explained. Like all strong acids, sulphuric acid reddens litmus paper or tincture of litmus; but the acid must be considerably diluted in order to manifest this change with effect, otherwise the destructive tendency of the acid comes into operation at once; the vegetable colour is charred and no redness is manifest.

Sulphuric acid has a great tendency to unite with alkalies, and the generality of metallic oxides—in short, all the substances to which the generic appellation, bases, is applied; constituting salts which are denominated sulphates.

Few substances admit of being determined, separated, and estimated with so great facility as sulphuric acid. The earth baryta, or its soluble combinations, is the test. Sulphate of baryta is absolutely insoluble in water, practically speaking; therefore, by means of baryta, or any compound of the metal barium (sulphate of baryta of course excepted), the whole of the sulphuric acid, whether combined or uncombined, existing in any solution may be easily thrown down. Of this the student may convince himself by a very simple experiment of the following kind. Pour about half an ounce of water into a beaker or test glass, add one drop of oil of vitriol, and prove the acidulous nature of the solution by moistening a slip of blue litmus paper with it. Next drop cautiously into the dilute acid a solution of caustic baryta as long as any white precipitate continues to subside. Neutralization being thus effected, the solution, formerly acid, will be found to have totally lost the property of reddening litmus; in other words, its acid contents will have been removed.

The mere occurrence, however, of a white precipitate on adding baryta to a solution, is not to be regarded as conclusive evidence of the presence of sulphuric acid: carbonic acid will effect that result, and some other acids as well; but all the white precipitates resulting are soluble in boiling nitric acid, with the sole exception of sulphate of baryta. Two white barytic precipitates, at least, not only dissolve in hot nitric acid, but dissolve with effervescence owing to the escape of gas. A barytic precipitate demeaning itself thus, may be either the carbonate or the sulphite. If the latter, a smell like that of a burning sulphur match will be recognizable; if the former, there will be, in small quantities, no smell whatever; in large quantities the peculiar odour of the gas (carbonic acid) which is evolved from soda water and ginger beer.

Not only are baryta and barytic compounds qualitative tests of the presence of sulphuric acid, but quantitative tests as well; for the sulphate of baryta is a definite compound, the amount both of barytic and of sulphuric acid which it contains is well known; hence the amount of sulphuric acid or of baryta may be readily determined in a definite quantity of dry sulphate of baryta. Every 108·5 parts of this body correspond with 40 of sulphuric acid, and 68·5 of baryta.

Hyposulphuric acid.—If a current of sulphurous acid be passed through water holding peroxide of manganese in suspension, the gas is absorbed whilst any of the peroxide remains, whether the solution be hot or cold; but the kind of decomposition differs according to the temperature at which the operation is conducted. If the water holding the oxide in suspension be cold, the following decomposition takes place:—Two equivalents of sulphurous acid combine with one equivalent of oxygen removed from the peroxide of manganese, which consequently is reduced to the condition of protoxide acid, and hyposulphate of protoxide of manganese results,—a decomposition which admits of being thus represented.

2 Sulphurous acid		1 Hyposulphuric acid	1 Hyposulphate of protoxide of manganese
1 Peroxide of manganese	1 Oxygen		
	1 Protoxide		

Or, in chemical symbols, as follows:—

$$MnO_2 + 2SO_2 = MnO.S_2O_5.$$

If the water holding the peroxide of manganese in suspension be heated, a still more complete absorption of oxygen is effected by the sulphurous acid gas; which becomes changed into sulphuric acid, and by uniting with protoxide of manganese, forms the sulphate of protoxide of manganese; or, as more simply expressed, the *protosulphate* of manganese. In this case only one equivalent of sulphurous acid reacts upon one equivalent of peroxide, and the scheme of decomposition is thus expressed.

1 Sulphurous acid		1 Sulphuric acid	1 Sulphate of protoxide of manganese.
1 Peroxide of manganese	1 Oxygen		
	1 Protoxide		

Or, $MnO_2 + SO_2 = MnO{\cdot}SO_3$.

Notwithstanding any care we may take in cooling the water holding the suspended oxide, it is difficult to prevent the formation of a little sulphate of manganese consentaneously with the hyposulphate; hence a process of separation must be had recourse to. The process is as follows:—The filtered liquor is decomposed by dropping in a solution of caustic baryta, which precipitates the protoxide of manganese, and generates the hyposulphate and the sulphate of baryta. The latter we have already seen to be a remarkably insoluble body, but the former is soluble; it accordingly passes through the filter, and may be obtained by continuous evaporation of the filtrate (filtered liquor).

If the hyposulphate of baryta be now re-dissolved in water, and sulphuric acid cautiously dropped in until no further precipitate is occasioned, it is evident we shall have succeeded in throwing down all the baryta, leaving a pure aqueous solution of hyposulphuric acid. The water may be dissipated by means of evaporation; but the evaporation must be conducted without heat, in a manner frequently employed by chemists when delicate solutions are concerned.

The aqueous solution being placed in a capsule of glass or platinum, is inclosed within the receiver of an air-pump in association with another capsule, holding strong oil of vitriol. A vacuum being now produced by working the pump, aqueous vapour arises from the dilute solution of hyposulphuric acid; and no sooner arises than it is laid hold of by the oil of vitriol, which becomes dilute at the expense of the former, and thus concentration of hyposulphuric acid is effected.

HYPOSULPHUROUS ACID.

This body has never yet been isolated; but its presence in combination with bases is unequivocally demonstrated. The results of these combinations are termed hyposulphites; and one of them, hyposulphite of soda, is now manufactured in considerable quantities for employment in photographic operations. There are various methods of producing hyposulphites; the following are the most important:—

(1). By boiling the solution of a sulphite with an excess of powdered sulphur, by which operation the necessary amount of sulphur to form a hyposulphite enters into combination. The solution now being filtered and evaporated, yields the hyposulphite pure.

(2). By the solution of zinc in a solution of sulphurous acid. This metal having a great tendency to unite with oxygen removes a portion from the sulphurous acid, generating hyposulphurous acid, which at once combines with the oxide of zinc, forming hyposulphite of oxide of zinc. By operating in this way, however, a variable amount of sulphite of zinc is simultaneously produced.

(3). By exposing solutions of alkaline sulphurets (sulphides) to certain oxidizing agencies—such, for example, as oxygen gas or atmospheric air.

(4). By boiling a solution of potash, soda, or baryta, with sulphur in excess. This process yields hyposulphite of the base, and persulphurets of the base radical: thus, supposing sulphuret of potassium to have been employed, we obtain hyposulphite of potash, and persulphuret of potassium.

Properties of Hyposulphites.—A hyposulphite may, in general, be known by the two following characteristics. It is decomposed on the addition of either of the mineral acids, with the evolution of sulphurous acid gas, easily recognizable by its peculiar smell, and deposition of sulphur; and if the hyposulphite be of an alkaline base it dissolves chloride of silver, forming a transparent sweet solution.

The remaining Oxygen compounds of Sulphur.—These are so devoid of importance, both theoretical and practical, that I do not think it desirable to treat of them in detail.

Combinations of Sulphur with Hydrogen.—There are two combinations of sulphur with hydrogen—namely, sulphuretted hydrogen, or hydrosulphuric acid, and bisulphuretted hydrogen.

SULPHURETTED HYDROGEN, OR HYDROSULPHURIC ACID.

Composition	HS
Atomic weight	17
Atomic or combining volume in the gaseous state . .	$\boxed{}$
Specific gravity in the gaseous state	1·1681

General Remarks.—This compound is an agent of great importance to the analytical chemist. It may be considered as the test *par excellence*, for calcigenous metals; all of which, except iron, manganese, cobalt, nickel, and uranium, precipitate from their solutions without any collateral aid, and even the five excepted metals are precipitated from their solutions by this agent in the presence of an alkali—by preference ammonia. The prevailing colour of these precipitates is black; but zinc yields a white precipitate, and it is the only metal which does so. Manganese (one of the metals which requires the collateral aid of an alkali to effect precipitation) yields a precipitate with

hydrosulphuric acid, which is sometimes called white, but which is in reality flesh or cream-coloured. Arsenic, cadmium, and tin (the latter in certain states of combination) are the only metals which yield a distinct yellow precipitate with it; the precipitate afforded by antimony is sometimes described as yellow, but it is in reality orange-coloured.

Thus, by the evidence of hydrosulphuric acid the analytical chemist gleans a vast amount of information. Let us suppose the existence of an unknown solution. It has to be analyzed. It yields a precipitate with hydrosulphuric acid, and, *therefore*, contains a metal; moreover, it contains a calcigenous metal, and the metal is neither iron, cobalt, nickel, manganese, nor uranium, for these only yield a precipitate when an alkali also is present. Again, the solution is black, therefore the metal can neither be arsenic nor cadmium in any state, nor tin, in at least one state (*i. e.* as a persalt), nor antimony. What a vast amount of information then is conveyed by this one test!

Preparation.—Direct union of sulphur with hydrogen has never yet been accomplished; but when sulphur is brought into contact with hydrogen in a nascent condition, combination between the two is readily effected. The preparation of hydrosulphuric acid is usually accomplished by acting upon sulphurets (sulphides) with sulphuric or hydrochloric acids. If hydrosulphuric acid be required absolutely pure, the most convenient sulphuret to employ is the sulphuret of antimony, and the best acid the hydrochloric (spirit of salt, or muriatic acid). The decomposition should be effected in a flask, heated by means of a spirit-lamp or other small flame; and the gas may be collected either over mercury or water—for although water dissolves from two and a-half to three volumes of the gas, the absorption soon reaches its maximum, and does not materially interfere with the pneumatic operation. It is but seldom, however, that the chemist requires to collect hydrosulphuric acid gas. In this and most other examples of the generation of a gas by the operation of heat on materials contained in a flask, it is proper to wash the gas in a little water: the means of accomplishing this will be soon described.

Theory of the Decomposition.—When sulphuret of antimony is acted upon by hydrochloric acid the decomposition is as follows:—The chlorine of hydrochloric acid, by uniting with antimony of the sulphuret of antimony, generates chloride of that metal, whilst the hydrogen of hydrochloric acid combining with sulphur of the original sulphuret of antimony forms hydrosulphuric acid. These several grades of decomposition are more readily explained by means of the following diagram:—

1 Sulphuret (sesquisulphuret) of antimony	3 Sulphur	3 Hydrosulphuric acid
	2 Antimony	
3 Hydrochloric acid	3 Hydrogen	
	3 Chlorine	1 Chloride (sesquichloride) of antimony

Or, $Sb_2{*}S_3 + 3HCl = Sb_2Cl_3 + 3HS$.

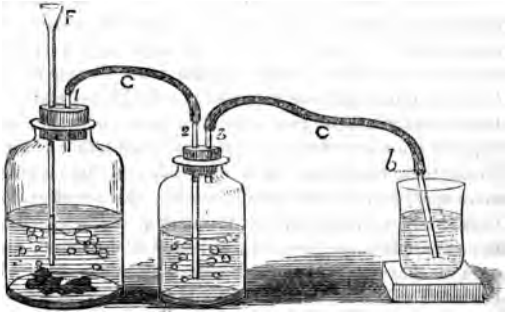
In general laboratory operations sulphuret of iron is more frequently used than sulphuret of antimony for developing hydrosulphuric acid, and oil of vitriol diluted with about three or four times its volume of water is substituted for hydrochloric acid. If the sulphuret of iron be completely free from particles of metallic iron, the resulting hydrosulphuric acid is equally pure with that resulting from sulphuret of antimony

* *Stibium*, the Latin word for antimony. *Vide* page 278.

and hydrochloric acid; but this seldom obtains; hence the gas is usually contaminated with a little hydrogen. The latter, however, is far from being prejudicial to the employment of hydrosulphuric acid—for most of its common applications is rather advantageous, by expanding the volume of the hydrosulphuric acid gas, and bringing it more fully into contact with the metal to be precipitated than otherwise would be the case.

As the operation of preparing sulphuretted hydrogen is of frequent occurrence in the laboratory, I shall proceed to indicate more fully than I have hitherto done the proper apparatus to be employed. In the process already detailed, involving the use of sulphuret of antimony and hydrochloric acid, we found it necessary to use a flask and to apply heat; but when sulphuret of iron is the material acted upon heat is no longer necessary, and, consequently, a wide-mouthed bottle may be substituted with advantage for the flask.

Thus modified, the apparatus will be as represented in the annexed cut. It consists of two wide-mouthed bottles; the greater of which may hold a pint, and the other need not be quite so large. The cork having been removed from the first, some pieces of sulphuret of iron are thrown in, and the cork is replaced. The smaller bottle is to be about half filled with water, and the cork replaced. 1 2 3 respectively indicate small lengths of glass tubing. C C are pieces of vulcanized india-rubber tube, one leading from the first to the second bottle,



another leading from the second bottle to the length of glass tube, which begins at the point marked *l*, and extends down into a beaker glass, which is supposed to contain a metallic solution to be precipitated by the hydrosulphuric acid gas. If we desire to set this apparatus in operation, nothing more is required than to pour oil of vitriol properly diluted down the funnel F, when, on coming into contact with the sulphuret of iron, hydrosulphuric acid will be liberated, and the latter bubbling through the water in the small bottle will be washed free from any sulphuric acid which may by chance have come over with it; and hydrosulphuric acid will be finally driven through the solution contained in the beaker glass. The apparatus here described differs in some respects from that commonly provided for the purpose, and unquestionably with advantage. Firstly, it is usual to substitute for the straight pieces of tubing 1 and 2 pieces bent once at a right angle, effecting the junction between them by a very short connector of india-rubber. It is usual, also, to substitute for the compound tube of glass and india-rubber terminating in the beaker glass one piece of bent glass tubing. Now the advantages of the apparatus above represented are as follow:—Complete absence of rigidity is secured between the two bottles—a somewhat important matter, as the operator will now discover, if he work much in the laboratory; complete freedom of motion in the delivery tube, and, what is still of more consequence, the ability to join at the point *b* a clean piece of

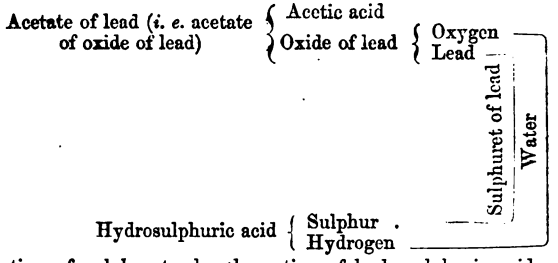
glass tubing for every new operation. Let us suppose that the chemist has been throwing down arsenic by means of the rigid bent delivery tube usually employed for this purpose. Of course the tube becomes soiled with the solution internally, and until perfectly cleaned ought not to be used for the precipitation of any other metal. But to clean a glass tube bent into the form of a V is no easy matter, and in trying to do so either time is consumed (without avail sometimes), or the operator is tempted to prejudice his result by using a dirty tube. Our form of apparatus removes all these difficulties. One word now concerning the sort of india-rubber tubing to be employed. It must be vulcanized, as I have already stated, and vulcanized india-rubber tubing can be obtained of almost any dealer in chemical apparatus; but the exact kind of vulcanized tubing which best suits our present purpose must be sought in a quarter not very congenial, for the most part, to philosophic operations. It must be sought at the tobacconist's under the name of *Hookah tubes*. It is not only a cheaper material than that purchased at chemical warehouses, or even of india-rubber manufacturers, but it is better in several respects, smaller, more delicate, and more easy of adaptation.

Sulphuretted hydrogen is either used as a mere qualitative test, to indicate the existence of certain bodies by the evidence of change of colour, or it is employed as a quantitative precipitant. In the former case it is generally preferable to employ a solution of the gas in water; in the latter the gas itself should generally be employed to avoid unnecessary dilution of the liquid acted upon. Water, to be impregnated with hydrosulphuric acid gas, should be pure and cold; it should, moreover, have been recently boiled to effect the expulsion of all traces of atmospheric air and other gases. Under these conditions water soon takes up its maximum of hydrosulphuric acid, the more speedily if it be agitated during the act of gaseous transmission. The solution thus obtained should be kept well corked and in a cool and dark place. Even with all this care it is decomposed in time, sulphur deposited, and the nauseous odour of rotten eggs, so characteristic of sulphuretted hydrogen, lost. Whenever these changes ensue the solution is worthless, and should be thrown away.

Though the usual condition of hydrosulphuric acid be gaseous, it may be also obtained in the liquid and solid state. It is liquified at ordinary temperatures by a pressure of about sixteen atmospheres, being condensed into a transparent liquid having the specific gravity of 0·9. Its reduction to the solid state requires the simultaneous application of extreme cold and pressure. Sulphurous acid gas is not a supporter of combustion for ordinary combustibles, but it readily burns if a light be applied, the results of combustion being sulphurous acid gas and water. It is a remarkably poisonous gas, a small percentage of it in the atmosphere being fatal to animal life if breathed many times in succession. Still more extraordinary is the fact that an atmosphere contaminated with this gas can prove fatal to animal life by mere absorption through the skin. A French veterinary surgeon demonstrated this by enveloping a horse in a large air-tight bag containing this gas mixed with air. The horse died from the effects of cutaneous absorption. Nevertheless, the gas is exhaled from the hair of animals, and this fact is taken advantage of in the employment of a hair dye. Formerly nitrate of silver was employed as the universal hair dye, but it is attended with the great disadvantage of discolouring skin as well as hair. A mixture of oxide of lead and lime is now employed, and it has the advantage of dyeing the hair without discolouring the skin. The theory of the application is simply this:—Lead being one of the metals with which hydrosulphuric acid yields a black precipitate, and the hair being well penetrated with the metallic oxide, blackness results from the decomposition of that oxide by the hydrosul-

phuric acid which it meets with in the capillary tubes. The function of the lime is not only to effect removal of oil, but to render the oxide of lead somewhat soluble.

It remains now for me to explain the nature of the precipitates thrown down by hydrosulphuric acid from certain metallic solutions. These compounds are sulphurets, otherwise called sulphides; the results of direct union, therefore, between sulphur and the metal, or other second body, as I have already explained, page 335. Consequently, when hydrosulphuric acid is passed through a solution of a metallic oxide, and a metallic sulphuret of the metal results, water also must be formed. The following diagram, illustrating the formation of sulphuret of lead by means of hydrosulphuric acid transmitted through acetate of oxide of lead, will render this statement evident:—



This production of sulphurets, by the action of hydrosulphuric acid on metallic oxides, is a very interesting subject for contemplation. Hydrosulphuric acid is the first hydrogen acid, or *hydr-acid*, that has hitherto come under our notice in this volume, and a slight amount of attention will assure us that its relations to bases are very different from the generally accepted relations of oxygen acids to the same. I say *generally* accepted, because chemists are by no means agreed concerning the exact scheme of the combination of the oxygen acids; but we speak of them at least as combining with bases, the latter being for the most part metallic oxides. Now let us contemplate the difference, as to scheme of combination, between the action of sulphuric acid and hydrosulphuric acid on one oxide—of lead for instance. If sulphuric acid be added to oxide of lead, or a solution containing it, a white compound (sulphate of oxide of lead, or sulphate of lead as, for brevity, it is sometimes called) is formed. Thus we have, or at least we appear to have, a direct combination of sulphuric acid and oxide of lead, thus:—

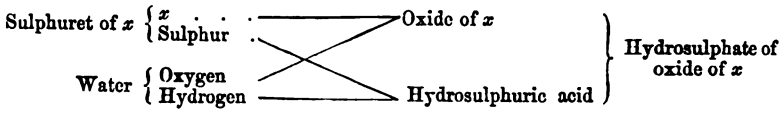
$$\left.\begin{array}{l}\text{Sulphuric acid}\\ \text{Oxide of lead}\end{array}\right\}\ \text{Sulphate of lead}$$

But if for sulphuric acid we substitute hydrosulphuric acid, the former type of combination is wholly departed from. We do not obtain hydrosulphate of oxide of lead, but sulphuret of lead and *water*. There can be no question about the formation of sulphuret of lead, because it falls and we obtain it bodily; but had it so happened that the result of transmitting hydrosulphuric acid through oxide of lead might have been a substance soluble in water, our chief evidence as to the formation of a sulphuret would have been absent. It might have dissolved as a sulphuret without decomposition of water, or as a hydrosulphate with decomposition of that fluid, as the two following schemes will explain.

SCHEME I.

$$\left.\begin{array}{l}\text{Sulphuret of } x\\ \text{Water . . .}\end{array}\right\}\ \text{Aqueous solution of sulphuret of } x$$

SCHEME II.



These remarks apply to all the hydracids without exception; and if we accept the Lavoiserian doctrine of salts, as being the results of union between acids (compounds) and bases (also compounds); and if, moreover, we continue to regard oxyacids as the type of normal acidity, the hydracids will constitute an intractable exception to such generalizations. But modern theory rather tends to the point of making hydracids the type, and associating salts of oxyacids with sulphurets, and other cognate bodies. There is no proper field in a volume of this kind for a full exposition of the arguments in favour of this doctrine or against it. I must, therefore, content myself with proving to the student by one example, that,—the attempt to assimilate oxyacid salts with the type of hydracid salts, is not so impracticable as one might imagine. Take, for instance, sulphuret of lead. Its elements are sulphur, oxygen, and lead combined, as chemists usually assume, in the grouping of three of oxygen plus one of sulphur (sulphuric acid) with one of oxygen plus one of lead (oxide of lead), or simply thus:—

Sulphuric acid }
Oxide of lead }

Or, still more simply, thus:—

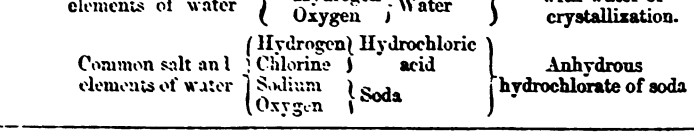
$$SO_3\ PbO$$

But it is also competent for us to assume the existence of a body having the following arrangement of elements:—

$$SO_4\ Pb$$

In which case the group SO_4 would correspond in function with sulphur in sulphuret of lead.

It would lead us too far from the objects of this volume were we to expatiate further on the theory of combinations; but, before quitting the subject, the curious fact may be noticed that if the strict notion of an acid, as adopted by Lavoisier, be advocated—if chemists see good reason for limiting the definition, *salt*, to the binary combination of a compound with a compound (an acid with a base), then must we be driven to the necessity of denying the claim of common salt to be a salt, inasmuch as both chemical analysis and chemical synthesis prove it to be a combination of the two elements, chlorine and sodium. Had it chanced to hold the elements of water in its crystalline structure, then we might have adopted one of two theories as to its constitution; we might have regarded it as a chloride plus water of crystallization, or as a hydrochlorate without, as the two appended schemes will illustrate—



Any theory requiring us to banish common table salt from the list of saline bodies, would indeed be startling; accordingly, when the real constitution of hydrochloric and the other hydracids became known, and the nature of the results of their action on bases determined, the term *haloid* salt was invented to designate bodies having a composition analogous to that of common table salt (from *αλς sea salt*, and *ειδος likeness*).

BISULPHURET OF HYDROGEN.

Composition	HS_2
Atomic weight	33

If flowers of sulphur be boiled with cream of lime (lime mingled with water), or a solution of potash or soda, a portion of sulphur is in either case dissolved, and numerous sulphurets are generated, the exact number and composition of which have never yet been determined. To these combinations of sulphur with lime, potash, or soda respectively, the designation of *polysulphurets* has been applied, a term indicative of the existence of an indefinite number of sulphurets. These polysulphuretted combinations are decomposed when poured into aqueous hydrochloric acid (spirit of salt). General turbidity of the mixture first ensues; but on allowing it to stand at rest for some time, a heavy yellow liquor (bisulphuret of hydrogen) sinks to the bottom, and may be withdrawn by syphonage. The substance decomposes when left exposed in the air, or when acted on by water; it may, however, be preserved if kept immersed in somewhat concentrated hydrochloric acid.

SELENIUM.

Equivalent or atomic weight . . . 39·5

Hitherto, all the elementary bodies which have come under our investigation are such as we find around us in large proportions. The immense quantity of oxygen existing in nature has been already noticed. Nitrogen and hydrogen exist also in large proportions; and sulphur is not only a widely-spread constituent of minerals, but it pervades our own bodies, and also the greater portion of the aliment we consume. Selenium comes before us in another guise. It is one of the rare substances which nature sparingly produced in the beginning; and when produced, hid it mysteriously in combination with rare mineral species, apparently with no other intention than to confer honour on the chemist who should discover it. That honour fell to the lot of the celebrated Jacob Berzelius, who discovered it in 1817.

If the student be sufficiently unwise to study the properties of selenium before he has made himself acquainted with other bodies more familiar to us, and more useful, he may obtain a specimen occasionally in the stores of those who deal in chemical curiosities; but quite as well, perhaps better, will it be to learn all that he wants to know concerning selenium, for a time, from the description now to be presented.

History and Natural History.—Selenium, so called after *σελήνη*, the moon, for the reason, more fanciful than philosophic, that it had been mistaken for tellurium, called after Tellus, the earth; and its identity with tellurium being disproved, it was named after the earth's satellite. It presents many points of similarity to sulphur, and in this does its chief interest lie; for selenium is a very interesting body, notwithstanding the chemical student has been advised to pass it over for a time with a casual investigation. Like sulphur, it can exist in the three conditions of solid, liquid, and gas. Like sulphur, it forms selenious and selenic acids, having a parallel composition to the

sulphurous and sulphuric. Then, again, selenic acid, like sulphuric acid, forms a very insoluble compound with baryta; and, for the most part, the crystalline character of seleniates is similar to the crystalline character of sulphates: hence they are said to be isomorphous. Furthermore, as sulphur unites with hydrogen to form hydrosulphuric acid, so does selenium unite with that element to form hydroselenic acid; and, as the former dissolves in water, yielding a solution which ultimately suffers decomposition, attended with the deposition of sulphur, so does hydroselenic acid afford parallel results. All these points are very curious and interesting, but we must not expatiate further upon them.

CHLORINE.

Equivalent or atomic weight	35
Atomic size or volume	□
Specific gravity in gaseous state	2·426

History and Synonymes.—Chlorine was discovered in 1774 by Scheele, who termed it dephlogisticated marine gas; subsequently it was called oxymuriatic acid, from the belief that it was a compound of muriatic acid (hydrochloric acid), plus oxygen. To our own countryman, Davy, the merit is due of pointing out its true nature, and referring it to the list of simple bodies. The modern appellation *chlorine* is very expressive and appropriate, being derived from χλωρός, *yellowish-green*, the exact tint of chlorine. Chlorine, although generally obtained as a gas, may be reduced to a liquid by pressure alone at ordinary natural temperatures, and still more readily by the simultaneous agency of cold.

Preparation.—As chlorine does not exist uncombined in nature, the chemist procures it artificially. Nature's great reservoir for chlorine is common salt (chloride of sodium), in comparison with which all other combinations of chlorine are insignificant. Chlorine is usually prepared by one of two processes: either by distilling a mixture of peroxide of manganese, common salt, and oil of vitriol, or a mixture of peroxide of manganese and hydrochloric acid. The second operation is, perhaps, less frequently performed than the first; but as the decomposition which ensues is somewhat the more simple, it shall first receive our attention. The decomposition is as follows:—

Hydrochloric acid . . .	Chlorine		is evolved.
	Chlorine . . .	Water	Protochloride of manganese.
	Hydrogen		
Peroxide of manganese	Oxygen		
	Manganese . . .		

From an examination of which scheme we see that the results of this decomposition are protochloride of manganese, water, and chlorine, of which alone the latter is gaseous at the temperature employed, and is therefore evolved. In symbolic notation the decomposition is thus represented:—

$$MnO_2 + 2HCl = MnCl + 2HO + Cl.$$

If for a mixture of hydrochloric acid and peroxide of manganese we substitute a mixture of sulphuric acid, peroxide, and common salt (chloride of sodium), the decomposition is as follows:—

1 Chloride of sodium { 1 Chlorine, 1 Sodium } Soda
1 Peroxide of manganese { 1 Oxygen, 1 Protoxide . .
1 Sulphuric acid → 1 Sulphate of soda.
1 Sulphuric acid → 1 Sulphate of protoxide (protosulphate) of manganese.

A decomposition represented by the following symbolic notation :—

$$NaCl + MnO_2 + 2SO_3 = NO \,.\, SO_3 + MnO \,.\, SO_3 + Cl.$$

Whichever process for the liberation of chlorine be adopted, the same arrangement of apparatus will suffice, and is represented in the subjoined diagram, the nature of which is so obvious that few words of explanation will suffice. A common Florence flask is the recipient of oxide of manganese and its decomposing associates, and the acid by which decomposition is effected is poured in through a little funnel, passing well down into the contents. The liberated chlorine may, probably, be contaminated with a little hydrochloric or sulphuric acid, and should therefore be washed by an interposed bottle containing a little water; from which, finally, by means of a properly-disposed tube of glass, gutta-percha, or vulcanized rubber, it may be conducted under the mouth of an inverted bottle standing over the shelf of the pneumatic trough.

CHLORINE WITH HYDROGEN (HYDROCHLORIC ACID).

Equivalent or atomic weight	36
Atomic volume	
Specific gravity	1·2474

History and Synonymes.—Hydrochloric acid, in its pure or gaseous condition, was discovered by Priestley in 1772; but its aqueous solution, known as muriatic acid or spirit of salt, has been prepared from times of great antiquity.

Preparation.—Process 1: The readiest means of preparing hydrochloric acid gas consists in the application of heat to its strong aqueous solution; in other words, spirit of salt or muriatic acid of the shops. This is how it was originally prepared by Priestley; the process, however, not being *instructive* as regards the composition of hydrochloric acid, I will now proceed to describe others.

Process 2. Hydrochloric acid gas may be synthetically formed by the combustion of hydrogen and chlorine mixed in equal volumes. The combustion may be effected either by means of the electric spark, or flame, or a red-hot body. Spongy platinum and solar light also produce a similar result. Chlorine and hydrogen mixed in the proportions necessary to generate hydrochloric acid may be retained in contact without union, provided light of the sun be excluded. If diffuse solar light be admitted, the combination ensues gradually; but if the light be direct, the result is combustion. According to Mr. Brande, the light of two charcoal points ignited by voltaic electricity produces a similar effect.

This process of generating hydrochloric acid gas is but of slight use in practice. Theoretically, however, it is most interesting and important. Not only does the operation teach us that hydrochloric acid is the result of direct union between hydrogen and chlorine, but it teaches us the ratio of that union, and, in addition, makes us acquainted with the important fact that the union is attended with no condensation. From this latter circumstance it follows that the atomic size of hydrochloric acid must be equal to two volumes, or ; as it is, indeed, represented at the commencement of our description.

It is important to remember, in connection with the preceding operation, that the hydrogen and chlorine gases employed may be absolutely deprived of aqueous moisture, and, as a consequence, of oxygen. Hence it follows that hydrochloric acid gas must be devoid of oxygen. At this epoch of chemistry it would be scarcely necessary to impress this fact on the learner's mind, except for the circumstance that the theory was once strenuously maintained that muriatic acid (hydrochloric) contained oxygen as a necessary constituent.

Process 3. By the distillation of dry common salt, mixed with a sufficient quantity of strong oil of vitriol to convert it into a thick paste. In conducting this operation, the common salt should be powdered, thrown into the distillatory vessel, and the necessary quantity of sulphuric acid added. A due pasty consistence may be imparted by merely shaking the flask or retort in which distillation is conducted. For the present operation a Florence flask answers perfectly well; and I shall now proceed to indicate a contrivance by which it may be adapted to our present wants with extreme ease.

When a flask is made to perform the function of a retort in distillatory operations, the usual plan of operation consists in supplying it with an accurately-fitting cork, perforated so as to admit of a bent glass tube. The fastidious craving of tobacco smokers for new contrivances has, however, brought into the market, under the name of *vulcanized rubber mouth-pieces*, a contrivance admirably adapted to abridge the trouble of chemists in this and numerous other operations. The mouth-pieces in question are elongated tubes of vulcanized rubber, as represented in the annexed sketch (Fig. A). One of these, having its large orifice moistened, may be readily adapted to a distillatory flask by drawing it over the mouth of the latter, as in Fig. B; and a piece of glass tube being thrust into the smaller extremity, a great deal of trouble in the way of cork-boring and tube-adapting

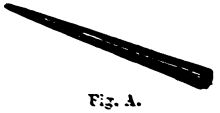


Fig. A.

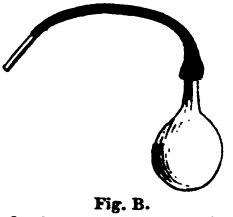
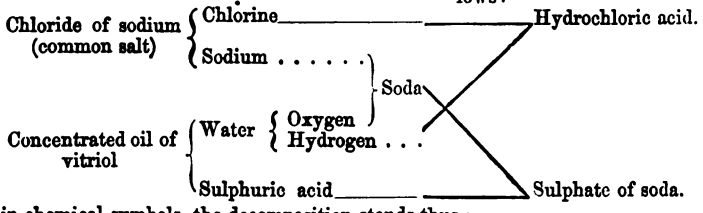


Fig. B.

is saved. Hydrochloric acid gas does not admit of being collected over water, inasmuch as this liquid absorbs it with great rapidity. It must be collected over mercury, or by displacement. The latter process serves well enough for all ordinary occasions, and the complete method of conducting the operation is represented in the annexed woodcut.

The decomposition which ensues in performing the preceding operation is as follows:—



Or, in chemical symbols, the decomposition stands thus:—

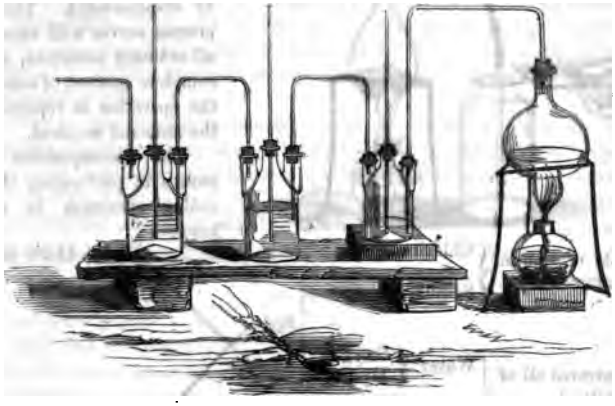
$$NaCl + SO_3 + HO = NaO . SO_3 + HCl.$$

Properties—Hydrochloric acid gas is colourless and exceedingly pungent. It is absorbed by water with violent rapidity, the result being hydrate of hydrochloric acid (the muriatic acid, or spirit of salt, of the shops). Owing to this violent tendency to unite with water, hydrochloric acid gas, though itself colourless, generates dense fumes when allowed to escape into the air; thus proving that the atmosphere, even in states of weather the most dry, contains variable amounts of aqueous vapour. Still more white and dense are the fumes which result when hydrochloric acid gas is brought into contact with gaseous ammonia, because of the hydrochlorate of ammonia (sal-ammoniac) formed. All burning bodies, when introduced into a vessel containing hydrochloric acid gas, are extinguished, and the gas itself cannot be made to inflame. Its specific gravity being 1·2474, and, therefore, the gas being heavier than atmospheric air, it may be collected by downward displacement, as I have already described.

Aqueous Solution of Hydrochloric Acid (*Spirit of Salt*).—This is a very useful compound in the laboratory and the manufacturing arts. It is prepared by a slight modification of the process employed for the generation of hydrochloric acid gas—that is to say, the same materials are employed, with the addition of water. A portion of the water should be mixed with the oil of vitriol and common salt, another portion being poured into a series of Woulfes bottles, and the whole connected as represented on the following page.

As regards the quantity of water to be employed in the preceding operation, and its disposition, the following remarks are to be attended to. The flask, instead of containing concentrated oil of vitriol and salt, should be charged, in addition to the salt, with a mixture of three parts oil of vitriol, by weight, and one part of water. The first Woulfes bottle in the series should contain just enough water to hold in

solution any traces of sulphuric acid which may come over. The two succ Woulfes bottles are about two-thirds filled with water, and their function is ev Their aqueous contents become gradually charged with hydrochloric acid ga may be put aside for use.



Although I have described the process for conducting the manufacture of sp salt on the small scale, yet experimental chemists but seldom make it. The com is prepared more economically on the large scale, being employed in many ind arts. Nevertheless, as iron vessels enter into the apparatus for its manufacture large scale, the resulting fluid is never pure. Instead of having a light straw-c as the pure acid should, it is more or less yellow, owing to the presence of chlo iron and free chlorine. In addition to these sources of impurity it also co traces of sulphuric and sulphurous acids, for which reason its purification is a ne before employment in conducting any delicate operation. The method of purif is as follows:—First determine whether free chlorine be present by pouring a li the suspected acid into a test tube, and immersing a fragment of gold-leaf; latter dissolve, the acid is contaminated by free chlorine; if the gold remain int free chlorine is present. It must be remembered, however, that free chlorine ca exist in solution of hydrochloric acid very recently prepared, inasmuch as ch when brought into prolonged contact with water, decomposes the latter, and be converted into hydrochloric acid. If sulphurous acid be present, it should be con into sulphuric acid, by the addition of that which we have just been engaged in away—chlorine. Chlorine, when passed through an aqueous solution cont sulphurous acid, speedily converts the latter into sulphuric acid by the decomp of water, as represented by the accompanying diagram:—

Chlorine _____ Hydrochloric acid

Water { Hydrogen / Oxygen } Sulphuric acid
Sulphurous acid

We next have to deal with the sulphuric acid. This may be separated by careful distillation; but a better plan consists in adding sufficient chloride of b to effect its complete precipitation. The impure spirit of salt having been tree

ibed, is next to be subjected to distillation, when pure aqueous solution of ɔchloric acid alone comes over, chloride of iron and sulphate of baryta being left ıd. Care should be taken to conduct the distillatory process very gently, and to before the residue in the flask, or retort, has become nearly dry, otherwise a chloride of iron, which is somewhat volatile at high temperatures, might come and contaminate the product.

: is frequently desirable to know the percentage amount of real hydrochloric acid specimen of spirit of salt. This may be exactly ascertained by learning the tity of marble (carbonate of lime) which it can dissolve. The results of a series ese operations, however, have been tabulated; and a reference to the table in ion is far more readily accomplished than a performance of the operation: for reason I append a tabulated statement of this kind.

Atoms of Acid.	Atoms of Water.	Real acid in 100 of the liquid.	Specific gravity.
1	6	40·659	1·203
1	7	37·000	1·179
1	8	33·945	1·162
1	9	31·346	1·149
1	10	29 134	1·139
1	11	27·206	1·1285
1	12	25·517	1·1197
1	13	24·026	1·1127
1	14	22·700	1·1060
1	15	21·512	1·1008
1	16	20·442	1·0960
1	17	19·474	1·0902
1	18	18·590	1·0860
1	19	17·790	1·0820
1	20	17·051	1·0780

Tests for Hydrochloric Acid.—I shall confine myself to a discussion of the tests of rochloric acid in aqueous solution, the characteristics of the gas having been ciently described already. Hydrated or aqueous hydrochloric acid (spirit of salt) is ıuid manifesting the peculiar pungent odour of the gas. It is devoid of bleaching ɔerties, and thus may be readily distinguished from an aqueous solution of chlorine; her will it, like aqueous solution of chlorine, dissolve gold-leaf. Nitrate of silver ds, when brought into contact with it, a white flocculent precipitate (chloride of er), not soluble in nitric acid, but readily soluble in ammonia.

Nitro-hydrochloric Acid (*Aqua-regia*).—A mixture of two parts by measure of strong it of salt with one part by measure of strong aquafortis, constitutes a liquid to ch the designation aqua-regia has been applied, owing to the property it has of olving gold. *Aqua-regia*, nitro-muriatic, or nitro-hydrochloric acid, is not a mical compound. No combinations of it with bases are known; but the results of als dissolved in it are simply *chlorides*. The solvent agency of aqua-regia depends ly upon chlorine, which is liberated from hydrochloric acid whenever a solution of latter in water is brought into contact with nitric acid.

Compounds of Chlorine with Oxygen.—There are five well-known compounds of

chlorine with oxygen, and the existence of others is suspected. The five compounds are as follow :—

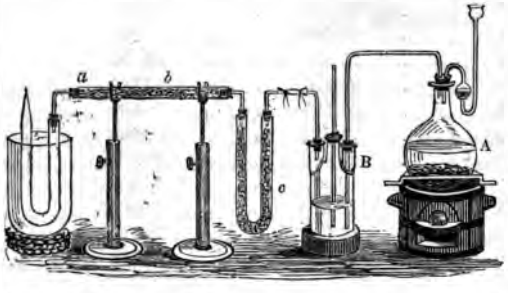
1. Hypochlorous acid (euchlorine) . .	$Cl.O$
2. Chlorous acid (protoxide of chlorine) .	$Cl.O_3$
3. Hypochloric acid (peroxide of chlorine) .	$Cl.O_4$
4. Chloric acid	$Cl.O_5$
5. Perchloric acid	$Cl.O_7$

HYPOCHLOROUS ACID.

Atomic weight	43
Atomic size	$\square$
Specific gravity	2·992

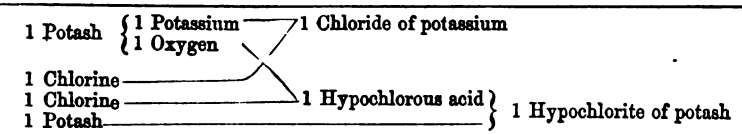
This compound was discovered by Sir H. Davy in 1811. He gave to it the name of *euchlorine*, and prepared it by the addition of hydrated hydrochloric acid (spirit of salt) to chlorate of potash. It is impossible, however, to generate hypochlorous acid pure by this means. The method of obtaining it absolutely pure is as follows :—

Chlorine being liberated in the flask A, is washed in the Woulfes bottle B, to effect the separation of hydrochloric or sulphuric acid, and is then passed through fragments of chloride of calcium, contained in the U-tube (*c*), and finally through peroxide of mercury in the tube *a b*, where the hypochlorous acid is generated, and passing on is received in a U-tube, maintained cool by a mixture of ice and salt. In order to avoid complication in the diagram, one important particular has not been taken cognizance of: the tube *a b* should be maintained cool by a constant stream of cold water. It is well, therefore, to surround it with a metallic sheath after the manner of the Liebig distillatory apparatus, already described in pages 303, 304.



Properties.—Hypochlorous acid thus prepared is an orange-coloured volatile liquid, endowed with strong bleaching properties, and readily decomposable by the agency of sufficient heat. It boils at a temperature of about 36° Fah. under the ordinary atmospheric pressure. Water dissolves about two hundred times its own volume of hypochlorous acid, the colour of which it assumes, as also its bleaching properties.

Aqueous Solution of Hypochlorous Acid and its Compounds.—If a current of chlorine be transmitted through a weak solution of an alkali or an alkaline earth, products, some of which are known in commerce as chlorides of the alkalies or alkaline earths, result. Thus we have the so-termed chloride of soda and of lime. They are not chlorides, however, but mixtures respectively of a chloride with a hypochlorite—that is to say, a direct union of chlorine with a base radical, and of hypochlorous acid with a base. Thus, for example, in the case of potash, through which a current of chlorine has been transmitted, the decomposition is of the following kind :—



Or in chemical symbolic notation thus :—

$$2KO + 2Cl = KO.ClO + KCl.$$

These alkaline and earthy mixtures of chlorides and hypochlorites constitute valuable bleaching compounds, which are much employed in various arts. Their bleaching agent is hypochlorous acid, which, however, does not admit of being liberated from them without decomposition, and collected separately. Aqueous solution of hypochlorous acid may be procured by pouring into a large flask containing chlorine, a mixture of peroxide of mercury, and water, rubbed up into a thin paste. The chlorine is immediately absorbed, and two distinct compounds result—oxychloride of mercury, which is insoluble in water, and hypochlorous acid, which is soluble in that liquid; we have, therefore, a ready means of obtaining hypochlorous acid in aqueous solution.

Chlorous Acid.—The existence of this acid is well established; but as it is not applied to any important use its full description may be omitted.

HYPOCHLORIC ACID.

History and Synonymes.—This compound was discovered by Sir H. Davy in 1815, and very shortly after by Count Stadion of Vienna. It was originally called peroxide of chlorine, but is at this time more generally termed hypochloric acid, perhaps somewhat incorrectly, inasmuch as its claims to acidity are by no means well established.

Preparation.—If concentrated oil of vitriol be added to a few fragments of chlorate of potash, decomposition of the latter ensues, bisulphate and perchlorate of potash remaining, and hypochloric acid, which is gaseous at ordinary temperatures and pressures, being evolved. *It is possible* to effect the decomposition in a small retort by the aid of a water bath, and to collect the hypochloric acid evolved; but I would by no means recommend the operator to be concerned in so dangerous an experiment. Hypochloric acid is very explosive, and its explosion is attended with much danger. The operator, therefore, had better content himself with decomposing a few fragments of chlorate of potash in a test tube, by the addition to them of a few drops of strong oil of vitriol. Hypochloric acid under ordinary atmospheric pressures and temperatures is a ruddy gas, of exceedingly irritating odour and explosive character. Subjected to the cold produced by a mixture of ice and common salt, it liquefies into an orange-coloured fluid, which boils at about 36° Fah.; and at a temperature considerably short of 212° Fah. (the boiling point of water) it explodes.

CHLORIC ACID.

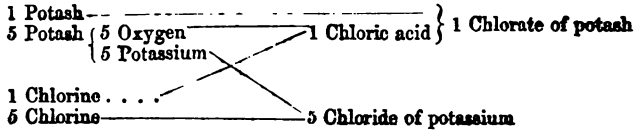
History, Synonymes, and General Remarks.—The existence of this acid was first indicated by Mr. Chenevix; but the credit of isolating it and obtaining it in a pure condition is due to M. Gay Lussac. The salts which it forms with bases are termed chlorates, but formerly hyper-oxy-muriates. The general similarity which obtains between chlorates, nitrates, iodates, and bromates, has already been adverted to.

Preparation.—Chloric acid is most conveniently prepared from chlorate of baryta,

from which, on the addition of sulphuric acid, all the baryta may be separated in the condition of sulphate of baryta, leaving the uncombined chloric acid in solution. Aqueous solution of chloric acid may be concentrated by simple heat until the acid acquires the consistence of a thin syrup; if the heat be pushed beyond this point decomposition of the acid ensues. The results of decomposition are chlorine, oxygen, and perchloric acid—that is to say, a portion of the oxygen, instead of being liberated, combines with a portion of chloric acid, and raises it to the higher state of oxygenation. Perchloric acid will be described hereafter.

Properties.—The most leading peculiarity of chloric acid and the chlorates is dependent on the facility with which they evolve oxygen. In this respect the analogy between chloric, nitric, iodic, and bromic acids—chlorates, nitrates, iodates, and bromates—is perfect. If pieces of paper be dipped into strong chloric acid, and dried, they take fire; if mixed with alcohol, the latter is converted into acetic acid: if sulphurous acid be transmitted through it, sulphuric acid is generated, and chlorine evolved. The most important salt of chloric acid is chlorate of potash, a substance which has frequently come under our notice as a source of oxygen. It remains now to state the process by which chlorates, combinations of chloric acid with bases, are formed in practice. They *may* be formed by the direct addition of chloric acid to the required base; but it has already been stated that chloric acid is obtained from a chlorate: hence the latter must precede the former in the routine of actual production.

The great sources of chloric acid and the chlorates are strong alkaline solutions treated with chlorine; of these, a strong solution of potash is of greatest importance, and, under the circumstances indicated, the decomposition is as follows:—



Or in chemical symbolic notation thus:—

$$6Cl + 6KO = 5KCl + KO.ClO5.$$

From a study of which it will be seen that when six equivalents of chlorine react on six equivalents of potash, the results are one equivalent of chlorate of potash and five of chloride of potassium: of these products, the chlorate of potash crystallizes at a less degree of concentration than the latter, and thus an easy means is furnished of separating the two.

PERCHLORIC ACID.

History and General Remarks.—This compound of chlorine and oxygen was discovered by Count Stadion of Vienna, who also determined its composition to be seven equivalents of oxygen united with one of chlorine. Perchloric acid is not only interesting on account of the large amount of oxygen it contains, but it is very useful in the course of analysis, as furnishing a good means of effecting the discrimination and separation of potash. This is accomplished by virtue of the remarkably insoluble salt (perchlorate of potash) which results from the combination of perchloric acid with the alkali in question.

Preparation.—By distilling perchlorate of potash at a temperature of about 284° Fah., and mixed with half its weight of sulphuric acid, diluted with about one-third of

water. Thus treated, white vapours arise from the retort; and when condensed in a receiver by the proper application of cold, they yield a solution of perchloric acid. Perchloric acid, notwithstanding the large amount of oxygen it contains, is not easily decomposed. It may be concentrated by heat, until it acquires a density of 1·65, and by mixture with strong sulphuric acid and distillation it may be even obtained in the condition of a solid.

Perchlorate of Potash.—We have already seen that perchloric acid is obtained by distilling perchlorate of potash with sulphuric acid; in reality, therefore, the manufacture of perchlorate of potash must precede that of perchloric acid.

Under the head of *hypochloric acid*, otherwise denominated peroxide of chlorine, the reader has been informed that when sulphuric acid is added to chlorate of potash, hypochloric acid is evolved, and two salts—perchlorate of potash and bisulphate of potash—remain. I have also stated (page 362) that perchlorate of potash is a very insoluble salt; it follows, therefore, that the perchlorate may be readily separated from the bisulphate by the process of washing; such, indeed, is the method adopted. A very natural question now probably suggests itself to the experimentalist:—If perchloric acid be obtained from perchlorate of potash, and if the latter be a collateral result of the preparation of *hypochloric acid*—how, considering the violently explosive qualities of the latter, can perchlorate of potash be generated in any quantity with safety? The best method of proceeding is as follows:—Pour the necessary quantity of sulphuric acid into a flat porcelain dish, and drop in the chlorate of potash, finely powdered, by small quantities at a time, having previously taken the precaution of affixing the sieve to the extremity of a long pole. In this way large quantities of perchlorate of potash may be made without danger.

It is also possible to obtain perchlorate of potash in another manner; but the operation requires great attention to seize the right instant at which to withdraw the source of heat. When chlorate of potash is exposed to heat, we have already seen (page 283) that oxygen gas is evolved, and chloride of potassium is left behind. Notwithstanding this final result, a great quantity of the chlorate is converted intermediately into the perchlorate of potash, a change which may be known to have happened by the contents of the distillatory vessel acquiring a certain pasty consistency, and the cessation, for a time, of the delivery of oxygen. If the source of heat be removed directly, the change in question is noticed: a large quantity of perchlorate of potash may be obtained from the saline contents of the flask or retort. The major portion of the bisulphate of potash admits of removal by a small quantity of hot water, which may be so apportioned that very little of the persulphate of potash is acted upon. Final purification of the perchlorate may be effected by dissolving the whole solid remnant in a sufficient quantity of boiling water, and allowing the solution to cool. During the cooling process the perchlorate of potash crystallizes, on account of its insolubility, and the bisulphate remains in solution.

Combinations of Chlorine with Sulphur.—The union of chlorine with sulphur may be readily accomplished, giving rise to several chlorides; of these, two—the protochloride and the dichloride—have been especially studied. Their respective compositions are as follow:—

	Chlorine.	Sulphur.
Protochloride of sulphur	1	1
Dichloride of sulphur	1	2

Both these are generated by bringing heated sulphur into contact with free chlorine.

If chlorine be in excess, the protochloride results; if sulphur, the result is the dichloride. None of these chlorides of sulphur are of sufficient importance to warrant further description.

CHLORINE WITH NITROGEN.

Only one combination of chlorine with nitrogen is known. Its composition is indicated by the formula NCl_3; it may, therefore, be denominated terchloride of nitrogen.

History and General Remarks.—Terchloride of nitrogen was discovered by M. Dulong in 1811, and possesses interest on account of the extreme violence of its explosive properties. In point of fact, it is the most dangerously explosive compound known to chemists.

Preparation.—Terchloride of nitrogen is generated by the mutual action of chlorine on a solution of ammoniacal salt. For this purpose, a solution of hydrochlorate of ammonia (chloride of ammonium, or sal-ammoniac) is generally employed, and the safest plan of generating the dangerous compound is as follows:—

Take a piece of sheet-lead, about fourteen inches square; bend up its edges so as to form a shallow dish capable of holding about a quart of strong solution of sal-ammoniac, heated to about 60° Fah. Before the dish is used, it should be moistened with strong oil of vitriol, and made hot over a few pieces of burning charcoal; then it should be well washed with distilled water, but not wiped, nor should it be touched internally either by the hand or any other body; finally an absolutely clean glass jar, containing chlorine gas, should be inverted in the leaden dish containing the solution of ammoniacal salt, and the whole allowed to stand at rest until the formation of oily-looking globules are observed. These globules are the dangerous terchloride of nitrogen, which are heavier than the generating solution, and will consequently sink down on the leaden plate, where they had better be allowed to remain. Directions are given in some books for effecting their removal by means of a glass syringe having a narrow beak. The operator had far better leave this untried, and content himself with exploding the terchloride in the leaden dish whilst still surrounded with liquid. For this purpose, he removes the glass receiver carefully, places the dish at a respectful distance from his person, and touches the globules of terchloride with the oiled extremity of a long stick. Violent explosion is the result of this treatment, and the leaden dish, if not broken, will be considerably twisted and distorted. Terchloride of nitrogen immediately explodes on being brought into contact with fixed oils, and the general run of substances to which the term *dirt* may be applied; hence the necessity of scrupulously cleansing the glass jar used in its preparation. It is not exploded, however, by contact with oil of vitriol; and since hot oil of vitriol destroys fixed oils, the *rationale* of our lead-cleansing operation will be obvious.

BROMINE.

Atomic weight	80
Atomic volume	$\square$

History, Etymology, and General Remarks.—Bromine was discovered in 1826 by M. Balard in sea-water from which common salt had been deposited by evaporation. It is very similar in properties and general relations to chlorine; than which, however, it is less energetic, and consequently may be displaced from its combinations by that element. Bromine, under ordinary atmospheric pressures and temperatures, is a ruddy, thick liquid. At a temperature of about 53° Fah. it boils, and when cooled down to

— 68° Fah. it freezes. The appellation bromine is derived from Βρῶμος, *graveolentia*, because of its strong disagreeable odour.

Preparation.—It has been already mentioned that bromine was obtained from sea-water from which common salt had been separated. The state of its existence in this liquid is in combination with sodium, magnesium, and some other bodies, constituting various bromides. From these bromides, bromine is immediately obtained by an operation precisely similar in its character to that followed in the preparation of chlorine, namely, distillation in contact with peroxide of manganese and sulphuric acid.

BROMINE WITH HYDROGEN (HYDROBROMIC ACID).

Atomic weight	81
Atomic volume	[| |]
Specific gravity	2·73

General Remarks.—The only known compound of bromine and hydrogen is the product of the union of one atom of each, termed hydrobromic acid; it is the exact analogue of hydrochloric acid, being, like this, a compound of one atom of each constituent, having the same atomic volume, and possessing the same general relations.

Preparation.—Inasmuch as hydrobromic acid is the analogue of hydrochloric acid, theory suggests that the same general scheme of treatment should suffice for the generation of both; practically, however, this is not quite the case, for although hydrobromic acid may be generated by heating a mixture of bromide of potassium and oil of vitriol, yet the result is never pure, being contaminated with water and sulphurous acid, as is illustrated by the appended diagram.

Hydrobromic acid	Bromine . .	Water
	Hydrogen . .	
Sulphuric acid	Oxygen . .	
	Sulphurous acid	

Or, in chemical symbols, thus—

$$HBr + SO_3 = SO_2 + HO + Br.$$

That is to say, no sooner is the bromide of potassium decomposed, and its hydrobromic acid liberated, than a portion of sulphuric acid still continuing to react, decomposes a portion of the hydrobromic acid, its hydrogen combining with oxygen of sulphuric acid to form water, and its bromine being set free.

Pure hydrobromic acid, however, may be obtained by decomposing bromide of phosphorus in contact with a little water. The reaction is represented in the subjoined diagram:—

Bromide of phosphorus	Bromine	Hydrobromic acid
	Phosphorus	
Water	Hydrogen	
	Oxygen	Phosphorous acid

Or by chemical symbolic notation as follows:—

$$PhBr_3 + 3HO = PhO_3 + 3HBr.$$

The generation of the necessary bromide of phosphorus and the production of hydrobromic acid are usually effected by one operation, as follows:—

A glass tube moderately thin, and having an internal diameter of about half an inch, is bent, as represented in the annexed cut. To one extremity is attached a plain cork, to the other a perforated cork, with small glass tube attached. A small piece of phosphorus is first dropped into the bend *d*, and some fragments of glass moistened with water are added in sufficient quantity to rise some distance up into the terminal leg of the glass tube. Bromine being now poured into the bend *b*, the cork at *a* is replaced. By the preceding arrangement we obtain a distillatory vessel of such kind that all volatile products must necessarily permeate the moistened glass before they can escape. If, then, heat be cautiously applied to the angle *b*, bromine will be volatilized, and coming into contact with phosphorus, will be immediately converted into bromide of phosphorus; but no sooner is the bromide of phosphorus generated than passing through the moistened glass it is decomposed, as represented in our preceding diagram, into phosphorous acid and hydrobromic acid; of these the former is at once dissolved and retained by the aqueous moisture, allowing the hydrobromic acid to make its escape. It may either be collected over mercury or by displacement.

Properties.—Hydrobromic acid is, under common temperatures and pressures, a colourless irritating gas, which fumes in the air like hydrochloric acid gas, and for the same reason. Chlorine immediately decomposes it with the formation of hydrochloric acid and the liberation of bromine; but if an excess of chlorine be employed, it unites with the liberated bromine, chloride of bromine being then the result.

Combinations of Bromine with Oxygen.—Whether there be more than one compound of oxygen and bromine is not well determined; but the only compound of these elements meriting our attention is the bromic acid.

Preparation.—Bromic acid is prepared from bromate of potash by a precisely similar treatment to that employed in the preparation of chloric acid from chlorate of potash, and the latter salt is generated by a process exactly like that followed in the generation of chlorate of potash, only substituting bromine for chlorine. Bromic acid is the analogue, both as regards composition and chemical properties, to the nitric, chloric, and iodic acids. Like these, each equivalent or atom contains five equivalents or atoms of oxygen; and its salts, like those of the other acids in this group, deflagrate when brought into contact with red-hot charcoal.

IODINE.

Atomic weight		127·1
Atomic or combining volume . . .		⊡
Specific gravity of solid iodine .	=	4·95
Specific gravity of iodine vapour .	=	8·716

History, Etymology, and General Remarks.—Iodine was discovered in the year 1812, by M. Courtois, a saltpetre manufacturer; but M. Gay Lussac and Sir H. Davy were the first to study its properties intimately, and to refer it to the proper place in the list of chemical bodies.

Iodine, at ordinary temperatures and pressures, is a dark coloured solid of metallic crystalline aspect, not unlike black-lead in general appearance. It fuses at 225° Fah., and boils at 347° Fah. Its vapour possesses a beautiful violet tint, from which characteristic the appellation iodine is derived (Ἰώδης, *violet-coloured*). The general similarity of iodine to chlorine and bromine, has already been remarked at pages 48-50.

Preparation.—Iodine is prepared from the iodide of sodium, potassium, or magnesium, in like manner as chlorine is prepared from corresponding chlorides of the same metals; in other words, by subjecting a mixture of the iodide with peroxide of manganese and sulphuric acid to distillation. Large quantities of iodine have been made commercially for many years past: the source of the iodides subjected to decomposition is the lixiviated fluid of burnt sea-weeds, from which all the carbonate of soda has been extracted by evaporation. Formerly, all the carbonate of soda (common soda) of commerce was obtained either from the lixiviated ashes of the salsola soda (barilla plant), or from the lixiviated ashes of sea-weeds; at present, however, it is more economically prepared by decomposition of sea-salt: nevertheless, sea-weeds continue to be burned, and their ashes lixiviated for the iodine which they yield.

Properties.—In addition to the properties of iodine already enumerated, there is a very important chemical characteristic by which it may be distinguished from all other substances: it colours starch blue. The test is very delicate, provided the necessary precautions be taken. The iodine must be free—that is to say, it must not be in the state of iodide, iodate, or any other compound form; and the solution containing it must be neither hot nor alkaline. Iodine is but slightly soluble in water, about one part in 7,000; nevertheless, the aqueous solution acquires a brown tint, and the characteristic smell and taste of iodine. It copiously dissolves in an aqueous solution of iodates and iodides, also in alcohol and ether.

IODINE WITH HYDROGEN (HYDRIODIC ACID).

Atomic weight	128·1
Volume	[ ] [ ]
Specific gravity	4·443

The only known compound of iodine with hydrogen is hydriodic acid, the analogue of hydrobromic and hydrochloric acids; consisting of one atom or equivalent of each of the elements, having the same atomic volume, and general chemical relations.

Preparation.—Hydriodic, like hydrobromic acid, does not admit of preparation by application of heat to a mixture of iodide of potassium and sulphuric acid: because, under these circumstances, the generated hydriodic acid is immediately decomposed, in accordance with the following scheme, expressed by a diagram, and in chemical symbols:—

$$\left.\begin{array}{l}\text{Hydriodic acid}\left\{\begin{array}{l}\text{Iodine}\\ \text{Hydrogen}\end{array}\right.\\ \text{Sulphuric acid}\left\{\begin{array}{l}\text{Oxygen}\\ \text{Sulphurous acid}\end{array}\right.\end{array}\right\}\text{Water}$$

$$HI + SO_3 = SO_2 + HO + I.$$

It is prepared by decomposing iodide of potassium, by contact with a small quantity of water, in a small tube retort, as here represented. Alternate layers of broken glass, moistened with water, iodine, and phosphorus, being passed into a tube of this kind, and heat being applied, decomposition ensues; iodide of phosphorus is no sooner formed, than meeting with water it decomposes the latter, hydriodic and phosphorous acid resulting. Of these, the latter remains dissolved in the water, whilst hydriodic acid passes over, and may be collected over mercury, or by displacement.

Properties.—Hydriodic acid as thus generated in a pure state is a colourless pungent gas, readily dissolved by water, and decomposed with extreme facility by chlorine, bromine, and even by the prolonged agency of atmospheric air.

Solution of Hydriodic Acid.—It is frequently necessary in practice to prepare an aqueous solution of hydriodic acid. This may be readily accomplished by transmitting a current of hydrosulphuric acid gas through iodine held in suspension by water. The decomposition is very simple: the hydrogen of the hydrosulphuric acid combines with iodine, and forms hydriodic acid, which is immediately dissolved in water, sulphur being simultaneously deposited. When no further iodine remains uncombined, the solution must be filtered to effect the removal of sulphur precipitated.

Combinations of Iodine with Oxygen.—Oxygen and iodine are known to unite in three proportions, as follow:—

(1)	Hypoiodic acid	IO_4
(2)	Iodic acid	IO_5
(3)	Periodic acid	IO_7

Iodic Acid.—The various operations already described as being necessary for manufacturing chloric acid, will yield iodic acid if we substitute iodine for chlorine. These operation are—(1) The generation of iodate of potash; (2) the decomposition of iodate of potash by chloride of barium, and the formation of iodate of baryta; (3) the decomposition of iodate of baryta by sulphuric acid cautiously added. These operations are of interest, as tending to prove a general similarity of relations between iodic and chloric acids; but if iodic acid in considerable quantities be required, the following more eligible process should be adopted:—Weigh out equal portions of iodine and chlorate of potash; mix them in a flask with five parts, by weight, of water, to which some drops of nitric acid have been added. On the application of heat to this mixture, chlorine is disengaged, and the iodine is converted into iodic acid. The decomposition is as follows:—The nitric acid begins by decomposing a proportionate quantity of chlorate of potash, nitrate of potash being generated and chloric acid liberated; but it is no sooner liberated than in its turn decomposed, yielding up its oxygen to a portion of iodine, forming iodic acid, and liberating chlorine. The iodic acid thus generated, acts like the nitric acid formerly added, decomposing a fresh portion of chlorate; and thus the decomposition of chlorate of potash proceeds until none remains. Finally, the whole of the potash originally contained in the chlorate is converted into iodate of potash, which may be crystallized by evaporation.

Periodic Acid.—This compound being of inferior interest need not occupy our attention.

IODINE WITH NITROGEN.

There is only one known combination of iodine and nitrogen; it is the *teriodide*, and is, therefore, represented by the formula NI_3.

Preparation.—By pouring aqueous solution of ammonia (hartshorn, or liquor ammoniæ) on iodine, allowing the mixture to stand at rest for about two hours, then filtering off the liquid, and collecting the solid result, which is the teriodide, on several pieces of filtering-paper, taking care that no one portion be larger than the dimensions of a small pea. This latter precaution is rendered necessary by the extraordinary explosive quality of the compound in question, which is perhaps the most readily explosive compound known to chemists, although its explosion is not attended with much danger.

When dry, the teriodide of nitrogen cannot be touched without explosion. Even the soft part of a feather suffices, or the act of throwing it upon the surface of water.

Combinations of Iodine, with Sulphur, and Chlorine.—There are probably several of these compounds; none of them have been much studied, and they are all of inferior importance.

FLUORINE.

Equivalent, or atomic weight	=	18·9
Equivalent, or atomic volume		☐ ?

General Remarks.—The somewhat common mineral, termed fluor spar, is the result of a binary union between the metal calcium and the non-metallic, simple body fluorine. Of fluorine in the uncombined state, very little is known, in consequence of the difficulty of providing vessels capable of retaining it. Not only does it dissolve glass with facility, but all the known metals; in point of fact, the only material capable of withstanding its solvent agency is fluor spar (fluoride of calcium), a material already so fully saturated with fluorine, that it cannot appropriate more. Accordingly, it may be generated by acting upon fluoride of silver by means of chlorine, in a vessel of fluor spar, when it is liberated under the condition of a transparent colourless gas, similar apparently, in its general relations to chlorine.

COMPOUND OF FLUORINE WITH HYDROGEN—(HYDROFLUORIC ACID).

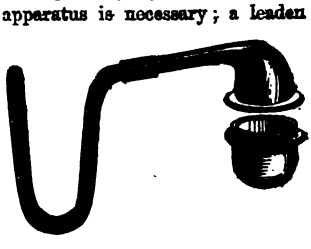
Equivalent or atomic weight	=	
Equivalent or atomic volume	=	☐☐ ?
Specific gravity of liquid acid		1·06

General Remarks—Fluorine and hydrogen are only known to unite in one proportion, constituting hydrofluoric acid, the exact analogue of hydrochloric, hydrobromic, and hydriodic acids. So long as the theory of Lavoisier, which assumed that the acidifying principle of all acids was oxygen, continued to be adopted, the compound under consideration was denominated *fluoric acid*, and that which we now term fluoride of calcium (fluor or Derbyshire spar) was denominated *fluate of lime*.

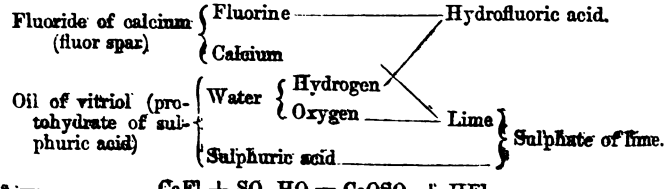
Preparation.—Anhydrous hydrofluoric acid must be prepared in vessels of lead or platinum: the former is usually employed from motives of economy. When liberated under ordinary atmospheric temperatures and pressures, hydrofluoric acid is gaseous; but by the application of a temperature of 32° Fah. (melting ice) it may be condensed

into a fluid. It frequently happens that hydrofluoric acid in the gaseous state is required, and for purposes not involving the collection of the gas. When this is the case the necessary apparatus is very simple, nothing more elaborate than a dish of lead or platinum being requisite. The preparation is thus conducted:—Finely powder some fluor spar, throw it into the leaden or platinum dish; pour upon it enough of concentrated oil of vitriol to form a thin paste, stir with a leaden rod, and apply heat. Gaseous hydrofluoric acid will be expelled. This form of operation enables the chemist to engrave, or rather etch, upon glass, and thus to render himself independent of the philosophical instrument-maker in the graduation of his tubes and other glass instruments. The operation of etching upon glass is the precise counterpart of etching on copper or steel, with the exception that hydrofluoric acid is used instead of nitric, and is used frequently, but not always, in the gaseous condition. The operation is commenced by smearing the glass surface to be operated upon evenly with a resinous compound known as etching-ground, or even common wax will do for small operations Upon this surface of etching-ground or wax the hydrofluoric acid exerts but little action, though it readily corrodes glass; if, therefore, the resinous or waxy coating be removed, the nature of the result will be obvious. The advantage of gaseous over liquid hydrofluoric acid for this operation is, that it effects an opaque corrosion, whereas the corroded surface produced by the latter is more transparent. When the piece of glass to be etched is flat, nothing more is required than to rest it on the basin, the surface to be engraved of course looking downwards; but if the glass be tubular, it must be suspended from a leaden cover by means of a wire, or strip of that metal.

Liquid Hydrofluoric Acid.—For the preparation of this a somewhat more complex apparatus is necessary; a leaden retort and tubular receiver, as represented in the accompanying diagram. The retort is made in two halves, of which the upper half fits into the lower by grinding, and the tube receiver is connected to the beak of the retort in a similar manner. The extremity of the tubular receiver is perforated with a little hole to permit the escape of the atmospheric air contained in the retort, and any small amount of hydrofluoric acid which may escape condensation. The tubular form of receiver is convenient for enabling it to be immersed in ice or snow, or, still better, a mixture of pounded ice or snow and common salt.



The theory of the decomposition is precisely analogous to that involved in the preparation of hydrochloric acid, and is, consequently, as follows:—



Or thus:— $CaFl + SO_3\,HO = CaOSO_3 + HFl.$

Operations with liquid hydrofluoric acid should be conducted with great care, as its action is most energetic on animal tissues, the smallest drop allowed to fall upon the

skin causing a dangerous burn, accompanied with extreme pain and much inflammation.

PHOSPHORUS.

Equivalent or atomic weight . . .	=	
Specific gravity of solid phosphorus .	=	1·77
Specific gravity of phosphorus vapour	=	4·326

History and Natural History.—Phosphorus was discovered by Brandt, a Hamburgh chemist, in the year 1669; but he kept his operation secret. Kunckel re-discovered it some days subsequently; but Gahn and Scheele, about 1769, were the first to produce it in large quantities. The great storehouse of all the elementary bodies we have hitherto discovered has been the mineral kingdom; but phosphorus is found in that division of nature very sparingly, the great source of its preparation being bones and animal fluids. Phosphorus may be obtained in the three physical conditions of solid, liquid, and gas; moreover, its solid form is subject to a curious allotropic variation, in which its physical, and many of its ordinary, chemical qualities are greatly modified. In this respect it resembles sulphur, the allotropic modification of which has already been treated of.

Preparation.—Phosphorus is at this time prepared in large quantities for the purpose of manufacturing lucifer matches; and the source from which it is obtained is bones, the solid portion of which, remaining after the prolonged operation of fire, atmospheric air being freely admitted, is, for the most part, basic, or superphosphate of lime—in other words, lime combined with an excess of phosphoric acid; the other solid constituent of bone earth (the term given to calcined bones) is carbonate of lime.

When this mixture of carbonate and superphosphate of lime is digested with oil of vitriol, decomposition ensues; the carbonate of lime is totally decomposed, sulphate of lime being formed, and carbonic acid expelled; the superphosphate of lime is, however, not decomposed entirely, sulphuric acid only combining with one portion of its lime; hence, instead of the superphosphate being converted into sulphate, the final result of its decomposition is *subphosphate of lime*—in other words, lime in combination with a diminished quantity of sulphuric acid. If we knew the exact proportions of sulphuric acid and lime, we might at once designate it by some definite chemical term; but, seeing that we do not, the term subphosphate of lime may be retained with advantage. Of the two compounds formed, the superphosphate of lime is alone soluble in water; it may be separated, therefore, by mere decantation. The superphosphate of lime being now evaporated to a syrupy consistence, powdered charcoal is intimately incorporated with it, and the mass completely dried; it is next packed into earthenware retorts, and distilled by strong furnace-heat, when phosphorus comes over, and must be collected under water.

As regards the theory of the operation, it is as follows:—The superphosphate of lime, on being exposed to violent heat in contact with charcoal, is decomposed into basic, or subphosphate of lime—which undergoes no further change—and phosphoric acid, which latter the charcoal decomposes, abstracting its oxygen, and liberating phosphorus, in accordance with the following diagram:—

$$\text{Phosphoric acid}\left\{\begin{array}{l}\text{Phosphorus}\\ \text{Oxygen}\end{array}\right. \\ \text{Charcoal (carbon)} \longrightarrow \text{Carbonic oxide.}$$

Or, in chemical symbolic notation, thus—

$$PhO5 + 5C = Ph + 5CO.$$

The phosphorus thus liberated is contaminated with many impurities; from a considerable portion of these it may be freed by straining, under hot water, through chamois leather; but its complete purity can only be insured by a second distillation.

Properties.—Phosphorus, in its ordinary solid condition, is a substance having the consistence of wax, almost colourless, and somewhat transparent when pure. It readily, however, acquires a tawny colour, and becomes coated with a fawn-coloured incrustation. This change is partly due to oxydation, and partly to the assumption of a peculiar molecular condition; for the fact is well established that phosphorus, if confined in vacuo, be exposed to light for sufficient time, it will become more or less coloured. Hence bottles, or other vessels containing it, should always be kept in a dark place, or be rendered opaque by pasting strips of paper, or other opaque material, around them. Phosphorus melts at about 111° Fah., boils at about 557°, and takes fire in an atmosphere of air or oxygen at about 140° Fah. Even when exposed to the air at ordinary temperatures, phosphorus undergoes a kind of slow combustion, evolving fumes which are luminous in the dark. Curiously enough, although ignited phosphorus burns in oxygen gas with great vigour, its slow combustion when enveloped in that medium does not ensue at temperatures less than 69° or 70° Fah. Phosphorus, as ordinarily procured by the process already indicated, is totally amorphous, or devoid of crystalline structure; it may be obtained in crystals, nevertheless, from certain solutions, of which the solution of phosphorus in bisulphuret of carbon is best. When this solution slowly evaporates, phosphorus is deposited in the form of rhombic dodecahedrons.

The Allotropic Condition of Phosphorus.—Under the head of sulphur, the allotropic condition of that body produced by throwing it, when fused at a certain temperature, into cold water, has been mentioned. If absolutely pure phosphorus be treated in the same way, a corresponding allotropic product is the result; but the operation is so much more difficult than with sulphur, that, practically, the method in question is ineligible. The most convenient method of generating allotropic or amorphous phosphorus, consists in exposing common phosphorus to a long-continued heat, of about 450° or 460° Fah., in a retort filled with some gas not capable of supporting combustion; for this purpose ordinary coal gas answers perfectly well. Thus treated, a portion of the phosphorus used distils over, but another portion is converted into a brick-red powder, and remains in the retort; it is allotropic or amorphous phosphorus, contaminated, however, with a little ordinary phosphorus, from which it may be separated by the solvent agency of bisulphuret of carbon, in which fluid the allotropic variety of phosphorus is insoluble. Allotropic phosphorus is generated in small quantities on sticks of ordinary phosphorus which have been for some time exposed to the air; formerly, the result was mistaken for an oxide of phosphorus: there is, however, no oxygen in its composition. Allotropic phosphorus differs from the ordinary material in several important chemical physiological and physical appearances. It is not soluble in sulphuret of carbon, as we have already seen; neither does it fuse under a temperature of 482° Fah., whilst ordinary phosphorus fuses at 79° Fah. At the temperature of 500° Fah. it re-passes to the condition of ordinary phosphorus. Ordinary phosphorus possesses a remarkable odour, whereas the allotropic variety is quite

inodorous. Ordinary phosphorus shines in atmospheric air at low temperatures; but allotropic phosphorus only acquires luminosity at the temperature of 392° Fah. and upwards. But perhaps the most remarkable evidence of the distinction between allotropic and ordinary phosphorus is of a physiological kind. Ordinary phosphorus is poisonous; hence the process of manufacturing those varieties of lucifer matches which contain it is very dangerous. Not only does it prove detrimental to the system when swallowed, but when its vapour is absorbed through the skin, or taken into the lungs. The characteristic symptom of slow poisoning by phosphorus is necrosis, or destruction, of the maxillary bones. People who suffer from carious teeth are particularly liable to suffer from this cause; and, consequently, in the French and German manufactories of lucifer matches, where common phosphorus is used, people with unsound teeth are not allowed to be engaged. Allotropic phosphorus is totally devoid of these poisonous qualities; it seems to be altogether innocuous: hence, abroad, it has to a great extent supplanted ordinary phosphorus in the manufacture of lucifer matches. In England, we do not seem to have been successful to an equal degree; English lucifer matches, for the most part, being manufactured with ordinary phosphorus.

Combinations of Phosphorus with Oxygen.—The existence of four compounds of phosphorus with oxygen is well established. They are as follow:—

(1) Oxide of phosphorus . . .	Exact composition unknown
(2) Phosphorous acid	PO_5
(3) Hypophosphorous acid . . .	PO_3
(4) Phosphoric acid	PO

Of these, the three acid combinations demand our extended notice, and more especially phosphoric acid.

PHOSPHORIC ACID.

Atomic or equivalent weight . . . 72

When phosphorus is burned in dry atmospheric air or oxygen gas, the vessel in which combustion takes place is dimmed with a white snowy powder, which collects about its sides; this white compound is anhydrous phosphoric acid. This compound is so exceedingly attractive of water that it combines with that fluid rapidly, and can never again be freed from one portion (an equivalent) of the water by any known process.

Although the hydrates (there are several) of phosphoric acid may be generated by dissolving the anhydrous acid in water, and subsequently applying heat and effecting evaporation to the necessary degree, this is not the best method in practice. The hydrates of phosphoric acid can be generated with more facility by boiling phosphorus and nitric acid together, in a tubulated retort, into the tubulure of which the undecomposed nitric acid is returned as often as it comes over.

The operation of applying heat and returning the undecomposed acid which comes over should be repeated until the whole of the phosphorus has disappeared. This point having been reached, the application of heat should be continued until the liquid acquires a syrupy consistence; when this change has ensued, the operation cannot be pushed any further in a glass vessel; all further concentration must be effected in a platinum dish. The hydrate of phosphoric acid having been transferred to a vessel of this kind is to be heated to fusion, by which means all the water, save one equivalent, is driven off, and the monohydrate of phosphoric acid results; it contains 11·2 per cent.

of water—that is to say, one equivalent. We have not hitherto had occasion to devote much attention to the hydrates of acids; but the hydrates of phosphoric acid involve an exceedingly curious philosophical point which will require notice in detail; each has sufficient permanence of composition to give rise to a specific class of salts. Sulphuric and nitric acids form, as we have seen, many definite combinations with water—real hydrates, in point of fact; but so little does the amount of water in combination alter the primary function of the acids in question, that the results of the combination of the acid of these hydrates with bases is in all cases the same. With the hydrates of phosphoric acid the result is different, as we shall presently see. The vitreous mass resulting from the treatment of phosphorus with nitric acid is a monohydrate of phosphoric acid, as I have already remarked—that is to say, it is a compound of one equivalent of phosphoric and one of water: hence its composition admits of being thus indicated, $PhO_5 + HO$. If this hydrate be mixed with a weight of water exactly equal to the quantity it has already, a second definite crystalline compound, bihydrate of phosphoric acid, results; its formula is, therefore, $PhO_5 + 2HO$. Finally, if the vitreous monohydrate of phosphoric acid be mixed with a quantity of water double in amount to that which it already contains, a crystallized trihydrate of phosphoric acid results, being indicated by the formula $PhO_5 + 3HO$.

Consequently we have demonstrated the existence of three hydrates of phosphoric acid. They are as follow:—

(1). Monohydrate of phosphoric acid . . . $PhO_5 + HO$
(2). Bihydrate of phosphoric acid . . . $PhO_5 + 2HO$
(3). Trihydrate of phosphoric acid . . . $PhO_5 + 3HO$

It is most accordant with what we know of these hydrates to regard the water as acting the part of a base; hence, instead of the expression, hydrate of phosphoric acid, we might say, perhaps with more propriety, *phosphate of water*, an expression which is indeed employed by some chemists. The preceding view is so far justified that the water may be replaced, wholly or in part, by recognised basic substances. Thus, there are three well known phosphates of soda: of these, the common phosphate of soda of the shops contains for each equivalent twenty-five equivalents of water. When the salt is gently heated, twenty-four equivalents of water readily fly off; but the remaining equivalent lingers with some pertinacity, thereby showing that it is in a different state of combination to the twenty-four equivalents; by increasing the heat, however, it may also be expelled, leaving an anhydrous salt containing two equivalents of soda and one of phosphoric acid. The salt thus produced is denominated the *bibasic variety* of phosphoric acid, in contradistinction to the phosphoric acid in the ordinary phosphate of soda, which is termed the tribasic variety. A comparison of the formulæ indicative of these substances will explain the nature of the distinction.

	Base.				
	Soda.		Water.		Phosphoric acid.
Common or tribasic phosphate of soda, containing common or tribasic phosphoric acid	2	+	1	+	1

	Base.				
	Soda.		Water.		Phosphoric acid.
Bibasic phosphate of soda containing bibasic phosphoric acid	2	+	0	+	1

Thus we have already two phosphates of soda, corresponding respectively with two of the three hydrates of phosphoric acid. There is also a third, or monobasic phosphate of soda. It is composed as follows:—

	Base.				
	Soda.		Water.		Phosphoric acid.
Monobasic phosphate of soda containing monobasic phosphoric acid.	1	+	0	+	1

And, of course, corresponds with the monohydrate of phosphoric acid already treated of. Frequently other appellations than those already mentioned are given to the three varieties of phosphoric acid. Ordinary or tribasic phosphoric acid is simply termed phosphoric acid; the bibasic variety is called *pyrophosphoric acid*; and the monobasic variety *metaphosphoric acid*. These acids, whether existing as hydrates, or in the condition of soluble salts, may be readily discriminated by their effects on soluble silver salts; the common, or tribasic variety of phosphoric acid, yields, with a soluble salt of silver—the nitrate, for instance—a yellow precipitate; the bibasic modification (pyrophosphoric acid), a white precipitate; the monobasic modification (metaphosphoric acid), a precipitate not only white but gelatinous. Solutions of mataphosphoric acid also have the property of coagulating albumen, whereas the others have not.

PHOSPHOROUS ACID.

Equivalent, or atomic weight . . 56

General Remarks.—When phosphorus is burned in oxygen gas or atmospheric air at ordinary pressures, phosphoric acid is the sole result, as we have already determined. If, however, a piece of lighted phosphorus be placed in a small dish under the receiver of an air-pump, and partial exhaustion be effected, phosphorous acid is the result. This process is so inconvenient, that it cannot be resorted to when large quantities of phosphorous acid are required; but it is suggestive of the means to be adopted for producing this substance.

Preparation.—(1). If phosphorus actually ignited generate phosphoric acid, when surrounded by attenuated air, it does not seem unreasonable to anticipate that phosphorus not actually ignited, but undergoing its usual change of slow combustion when surrounded with air of ordinary density, should also generate the same substance. Accordingly we find that large quantities of phosphorous acid may be generated by partially immersing sticks of phosphorus in a vessel of water, and allowing free access of air. Under these circumstances phosphorous acid is formed, and rapidly dissolving in the water, gives rise to a sour solution of hydrated phosphorous acid. Nevertheless, the phosphorous acid thus generated is not pure; it is contaminated with some phosphoric acid, into which phosphorous acid eventually changes when exposed in contact with water to atmospheric influences. For many purposes in the arts and manufactures the presence of this admixed phosphoric acid is of no consequence. This is the case with the anastatic process of copying letter-type and engravings. If, however, phosphorous acid be required pure, another method of preparation must be adopted, which is as follows:—

(2). When protochloride of phosphorus, $PhCl_3$, is added to water, mutual decomposition ensues, resulting in the formation of phosphorous and hydrochloric acids, as represented by the accompanying diagram.

1 Protochloride of phosphorus	1 Phosphorus	1 Phosphorous acid.
	3 Chlorine . .	
3 Water	3 Oxygen. . .	
	3 Hydrogen .	3 Hydrochloric acid.

The liquid holding these two acids in solution being concentrated to the density of a syrup, all the hydrochloric acid is evolved, and only the phosphorous acid, dissolved in water, remains. By the mere application of heat, the solution of phosphorous acid does not admit of being further concentrated; but if the solution be placed over a dish of oil of vitriol, in the receiver of an air-pump, and the air exhausted, a further amount of water may be removed, and phosphorous acid obtained as a crystalline hydrate, having the composition of $PhO_3 + 3HO$.

HYPOPHOSPHOROUS ACID.

Atomic or equivalent weight 40

Preparation.—When phosphorus is boiled with solutions of the fixed alkalies or alkaline earths, a hypophosphite of the oxide of the alkali or alkaline earth results. If baryta be the alkaline earth employed, a ready means of obtaining hypophosphite of baryta is suggested by cautiously adding the amount of sulphuric acid necessary to throw down the whole of the baryta. This operation furnishes a weak aqueous solution of hypophosphoric acid, which may be concentrated by heat up to a certain point without the occurrence of decomposition, but which does not admit of yielding the acid in a crystalline form.

The leading characteristic of hypophosphoric acid is its tendency to unite with oxygen; thus, when brought into contact with the oxides of mercury, copper, and some other metals, oxygen is removed, the metal is reduced, and the hypophosphorous acid is raised to the condition of phosphoric acid.

OXIDE OF PHOSPHORUS.

Composition uncertain.

For a long time the opinion was entertained that the red powder which forms during the combustion of phosphorus in oxygen or atmospheric air was a true oxide of phosphorus; but we have already seen that the compound in question is chiefly composed of phosphorus in its second, or amorphous, or allotropic condition. Nevertheless, a portion of oxide of phosphorus is actually present; but it may be prepared more pure, and in larger quantities, by the following method:—

Preparation.—Into a test-glass, containing a stick of phosphorus, pour hot water, by which treatment the phosphorus melts. Now transmit through the fused phosphorus a current of oxygen gas. Combustion ensues, and the water becomes pervaded with red particles. This red material is a mixture of oxide of phosphorus with uncombined phosphorus; and the latter being separated by sulphuret of carbon, oxide of phosphorus remains.

Combinations of Phosphorus with Hydrogen.—Chemists are acquainted with three compounds of phosphorus and hydrogen. The first is a gas, the second a liquid, and the third a solid.

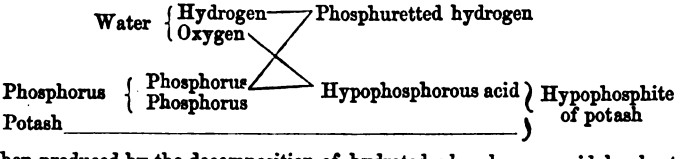
GASEOUS PHOSPHURETTED HYDROGEN.

	Phosphorus.		Hydrogen.
Composition	1	+	3
Equivalent or atomic weight . .		35	
Equivalent or atomic volume . .		[ ][ ]	
Specific gravity		1·185	

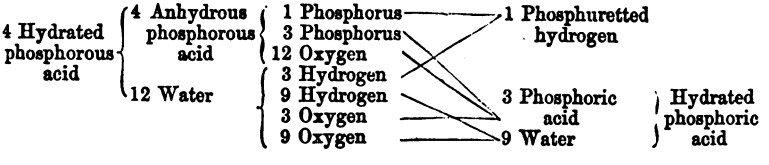
When phosphorus is heated in a retort completely filled, both body and neck, with aqueous solution of potash (liquor potassæ), the beak of the retort being plunged underneath the surface of liquor potassæ contained in a small pneumatic trough, the operation soon determines the escape of gaseous bubbles, which take fire spontaneously in the air. A similar phenomenon is also observed when lumps of phosphuret of lime are projected into water, or when hydrated phosphorous acid is decomposed by heat.

The inflammable bubbles under consideration are mainly composed of gaseous phosphuret of hydrogen (phosphuretted hydrogen), but they also contain variable amounts of liquid phosphuretted hydrogen, to the presence of which their quality of spontaneous inflammability at temperatures below 212° Fah. is due. By passing the spontaneously inflammable gas through a U-tube, surrounded by a mixture of snow or pounded ice and salt, the liquid compound condenses, and the gaseous combination is transmitted pure. The liquid phosphuret of hydrogen is exceedingly prone to decomposition. It can only be retained unchanged at a low temperature, and in a dark place. Under the influence of light it decomposes, gaseous phosphuretted hydrogen being generated, and the third or solid phosphuret of hydrogen indicated above.

The generation of phosphuretted hydrogen by the mutual decomposition of potash solution and phosphorus, is explained by the following diagram :—



When produced by the decomposition of hydrated phosphorous acid by heat, the decomposition is as follows :—



PHOSPHORUS WITH NITROGEN.

There is a compound of phosphorus with nitrogen, having the composition of N_2P. It is a white solid body, characterised by much stability, neither being decomposed at a red heat, nor acted upon by acids or alkalies. Such an amount of stability is remarkable for a nitrogen compound, most of which are characterised by facility of decomposition.

PHOSPHORUS WITH SULPHUR.

When phosphorus is brought into contact with sulphur, and both gently heated, combination readily ensues. Several phosphurets of sulphur may, in this way, be generated by varying the quantities of the two substances. Chemists are not agreed as to the number or the composition of these phosphurets of sulphur. Their most remarkable quality is that of extreme inflammability; more so than pure phosphorus. Before the introduction of lucifer matches, bottles, containing a mixture of these phosphurets of sulphur, were employed as a means of obtaining a fire extemporaneously.

PHOSPHORUS WITH CHLORINE.

There are two known compounds of phosphorus with chlorine, corresponding respectively with phosphorous and phosphoric acids. They are denominated protochloride and perchloride of phosphorus respectively, and their composition is indicated by the following formulæ:—

Protochloride of phosphorus . . .	$Ph\ Cl_3$
Perchloride of phosphorus . . .	$Ph\ Cl_5$

PROTOCHLORIDE OF PHOSPHORUS.

Atomic or equivalent weight	=	67
Atomic or equivalent volume	=	[ ]
Specific gravity of vapour	=	4·744
Specific gravity in liquid state	=	1·45

Preparation.—(1). By transmitting a current of dry chlorine over the surface of phosphorus contained in a small tubulated glass retort communicating with a receiver. The retort must be maintained hot during the operation, almost to the boiling point of phosphorus, and the receiver carefully cooled by a stream of water, or by immersion in ice. It is an essential condition to the success of this process that the phosphorus be always in excess over the chlorine; hence the transmission of gas must be stopped before the whole of the phosphorus has been appropriated, otherwise perchloride of phosphorus will also result.

(2). By transmitting the vapour of phosphorus over fragments of calomel in a glass tube strongly heated.

Properties.—A limpid fluid, which boils at 172° Fah., possesses a density of 1·45. and, when thrown into water, yields a solution of hydrochloric and phosphorous acids, Hence is furnished a ready means of generating phosphorous acid in a state of purity (page 375).

PERCHLORIDE OF PHOSPHORUS.

Preparation.—By transmitting chlorine through the protochloride.

Properties.—A white crystalline body easily volatilized, and furnishing, when brought into contact with water, an aqueous mixture of hydrochloric and phosphoric acids. The decomposition may be thus represented:—

1 Perchloride of phosphorus	5 Chlorine 1 Phosphorus	5 Hydrochloric acid
5 Water	5 Hydrogen 5 Oxygen	1 Phosphoric acid

Or in chemical symbols thus :—

$$PHCl_5 + 5HO = PhO_5 + 5HCl.$$

BORON.

Equivalent or atomic weight . . = 10·9

History and Natural History.—Boron was discovered by Sir Humphry Davy. It never exists in nature uncombined, but is found in combination with oxygen as native boracic acid, or united with soda, constituting the salt known as biborate of soda, or borax. Native boracic acid is found in the water of certain volcanic regions in Tuscany. Native biborate of soda is obtained from certain parts of Thibet and India. It is known in commerce by the name of tincal.

Preparation.—(1). By heating powdered fused boracic acid in a glass tube with a fragment of potassium, a part of the boracic acid is thereby decomposed—potash being formed and boron liberated. The undecomposed portion of boracic acid, by combination with potash, yields borate of potash. As a result of this treatment we have, therefore, a mixture of borate of potash and boron ; by treatment with water the former is washed away, and the latter obtained pure.

(2). By heating in an iron vessel the double fluoride of boron and potassium with metallic potassium, and digesting the residue with cold water, which dissolves all except the boron.

Properties.—Boron is a greenish powder, devoid of lustre. When heated in the air it readily takes fire, absorbs oxygen, and becomes converted into boracic acid.

BORON WITH OXYGEN (BORACIC ACID).

Equivalent or atomic weight . . 34·9

Boracic acid is the only known compound of boron and oxygen. It contains one equivalent of boron united with three of oxygen: hence its formula is BO_3.

Preparation.—(1). The native boracic acid of Tuscany is found associated with many impurities, from which it may be separated by solution and re-crystallization ; hence, this process furnishes us with one method of obtaining boracic acid.

(2). By the decomposition of biborate of soda (borax). A solution of this salt in water is readily decomposed by sulphuric or hydrochloric acid, an alkaline sulphate, or chloride, being formed, and boracic acid deposited. In either case the solution of borax should be hot and concentrated ; about one part by weight of borax to two and a half of water constitutes a good proportion. As the solution cools the acid crystallizes out as a hydrate, and may be separated almost pure ; if required completely pure, they must be re-dissolved in water, and re-crystallized.

Properties.—Boracic acid, as crystallized from aqueous solutions, is a hydrate, each equivalent containing three equivalents of water, or 43·6 per cent. When strongly heated, the whole of the water is evolved, and the anhydrous acid fuses into a sort of glass, which has the property of dissolving and rendering fusible the greater number of metallic oxides, each of which tinges the glass with its own characteristic colour. The increased degree of fusibility conferred on metallic bodies by boracic acid and borax, is frequently taken advantage of in the arts and manufactures, and the consideration of this property renders intelligible the generic expression *flux*, frequently applied to borax and some other bodies.

BORON WITH CHLORINE (CHLORIDE OF BORON).

Equivalent or atomic weight . . = 115·9

Equivalent or atomic volume . . = [ ][ ]

Specific gravity . . . = 4·035

There is only one known combination of chlorine and boron; it is the terchloride, being represented by the symbol $BoCl_3$, and therefore corresponds with boracic acid.

Preparation.—(1). By heating boron in an atmosphere of chlorine. (2). By exposing to heat in a porcelain tube a mixture of boracic acid with charcoal, and transmitting through the materials a current of dry chlorine gas.

Properties.—A colourless gas at ordinary temperatures and pressures, which fumes when allowed to escape into the atmosphere, owing to the decomposing agency of aqueous moisture, hydrochloric and boric acid being simultaneously generated.

BORON WITH FLUORINE (FLUORIDE OF BORON).

Equivalent or atomic weight = 67·5

Equivalent or atomic volume = [ ]

Specific gravity . . . = 2·37

Preparation.—By strongly heating, in a porcelain retort, a mixture of two parts fluor spar, and one part fused boracic acid. One portion of the boric acid is by this treatment decomposed. Its oxygen, uniting with calcium, forms lime, which uniting with some undecomposed boric acid, forms borate of lime, whilst a portion of fluorine uniting with boron, gives rise to fluoride of boron.

In symbolic notation the decomposition is thus represented :—

$$2BoO_3 + 3CaFl = BoFl_3 + BoO_3.3CaO.$$

Properties.—A colourless gas, with strong acid reaction, and a suffocating odour. Its leading characteristic is intense avidity for water; hence, dry organic matter, such as wood, starch, &c., made up of carbon, and the elements of water (oxygen and hydrogen), are rapidly charred by immersion in this gas, the elements of water being removed, and the carbon left. 700 or 800 volumes of fluoride of boron (fluoboric acid gas) may be dissolved in one volume of water without decomposition; but if the solution be concentrated beyond this extent, decomposition ensues, and the solution of another acid (the hydrofluoboric) results. The exact composition and relations of this acid still remain undetermined.

SILICON (SOMETIMES TERMED SILICIUM).

Equivalent or atomic weight = 21·3.

General Remarks.—Although silicon in its pure state is only produced by refined chemical operations, silica, or flint, is one of the most common substances in nature.

Preparation.—(1). By heating a mixture of silicic acid and potassium. The potassium removes oxygen from silicic acid, becomes potash, and liberates silicon, which may be isolated by dissolving away the associated potash with water.

(2). By heating a mixture of the double fluoride of silicon and potassium with potassium, and lixiviating the residue. The operation admits of being conducted in a

tube of German or other difficultly fusible glass. The theory of the decomposition is as follows:—

Double fluoride of silicon and potassium {Fluoride of potassium / Fluoride of silicon {Silicon / Fluorine} Fluoride of potassium}
Potassium

$$3KFl.2SiFl_3 + 6K = 9KFl + 2Si.$$

Properties.—Silicon is a brown powder, devoid of all metallic lustre, and infusible at high temperatures. If it be heated in oxygen gas or atmospheric air, oxygen is absorbed, combustion ensues, and silicic acid results.

SILICON WITH OXYGEN (SILICA, OR SILICIC ACID).

Equivalent or atomic weight . . . . . 45·3

Chemists are acquainted with only one compound of silicon with oxygen: it is the well-known substance silica, or silicic acid. Rock crystal is crystallized silicic acid almost pure; flint is the same acid uncrystallized, and contaminated with variable amounts of impurities. United with alumina and oxides of various metals, it constitutes the clays, and by far the largest portion of rocks. Rock crystal, beautifully crystallized, occurs in the Cornish slate formations; the crystals are locally known as Cornish diamonds. Specimens of rock crystal are frequently mistaken for diamonds by the inexperienced; but discrimination between the two is easy—the crystalline form of the diamond appertaining to the tessular or cubic system, and that of rock crystal to the rhombohedral.

Preparation.—Rock crystal may be regarded as pure silicic acid; but we may also liberate the latter pure from any state of siliceous combination by adopting either of the following processes:—

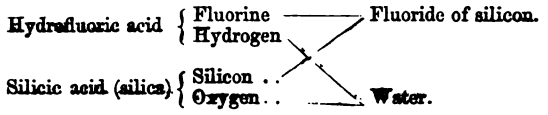
(1). Having powdered some glass or siliceous sand, mix the powder intimately with not less than three times its weight of carbonate of potash or soda. Fuse the whole in a platinum crucible, and dissolve out the fused result by water. The solution will be found to contain a gelatinous looking material, which is hydrated silicic acid. When thus recently prepared, silicic acid is partially soluble in acids and alkalies; by evaporating the alkaline solution to dryness, however, it is rendered insoluble by all acids, except the hydrofluoric. Following out this indication, our alkaline mixture is to be evaporated to dryness, and weak hydrochloric acid added, for the purpose of dissolving away the alkali and collateral metallic impurities. The final residue is silicic acid.

This operation is of great importance collaterally. It is the first stage of the analysis of a siliceous mineral, or an artificial siliceous compound. In conducting the analysis of glass, for example, it is necessary to dissolve the glass. This solution is effected by powdering it, fusing it with the carbonate of an alkali, or, in certain cases, a pure alkali, and isolating the silica as already described.

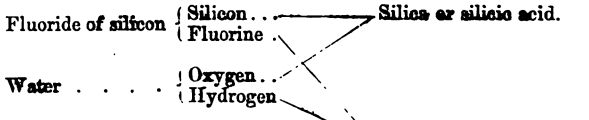
(2). Equal parts of fluor-spar (fluoride of calcium) and powdered glass being mixed, the mixture is formed into a pasty consistence with oil of vitriol, and distilled in a glass retort, the beak of which bends down into a glass containing quicksilver and water; gaseous fluoride of silicon bubbles through the quicksilver, and is decomposed on touching the water, generating silica and hydrofluosilicic acid. Inasmuch as the fluoride of silicon possesses such an intense affinity for water, the layer of mercury just

described is absolutely necessary to prevent the water of the receiving vessel running back into the distillatory retort and fracturing it.

The decomposition which ensues when powdered silica, fluor-spar, and sulphuric acid are distilled together, is represented by the accompanying diagram :—

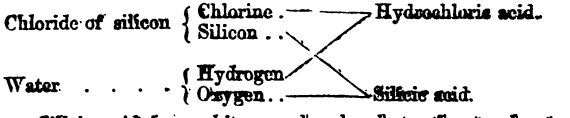


And the decomposition which ensues when the fluoride of silicon comes in contact with water is as follows :—



The hydrofluosilicic acid generated combines with water, and is obtained in solution. It is a valuable test, serving to distinguish potash from soda—the former yielding a precipitate with it, but the latter none.

(3). *By bringing chloride of silicon into contact with water.*—When chloride of silicon, a compound soon to be described, is brought into contact with water, a decomposition ensues of the following kind :—A portion of the water yields up hydrogen to the chlorine of the chloride of silicon, and generates hydrochloric acid gas, which remains in solution, whilst the liberated silicon, uniting with nascent oxygen, forms silicic acid, which deposits. The decomposition is represented by a diagram as follows :—



Properties.—Silicic acid is a white powder, harsh to the touch, tasteless, and inodorous. When recently liberated from its combinations in aqueous solution, it occurs as a gelatinous mass, which is a hydrate of silicic acid. In this condition it is soluble in water, alkalies, and many acids; but if the hydrate be heated, either alone, or mixed with its acid or alkaline solvent, to dryness, it is rendered insoluble in alkalies and all acids except the hydrofluoric.

Determination of Composition on Analysis.—On account of the few definite combinations of silicon and silicic acid, every statement as to the atomic composition of the latter acid must involve a certain amount of hypothesis. The percentage amount of silicon and oxygen in silicic acid is sufficiently easy to determine as follows :—When chloride of silicon is brought into contact with water, decomposition of the chloride, as we have recently seen, ensues, hydrochloric and silicic acids being the results. From this experiment the percentage composition of silicic acid is proved to be—

Silicon	47·66
Oxygen	52·34
	100·00

The majority of chemists consider, for reasons unnecessary to detail here, that silicic acid is a compound of three equivalents of oxygen plus one of silicon. If this assumption be correct, the atomic weight of silicon will be 21·3, the number which has been adopted in this treatise; and the chemical symbol for silicic acid will be SiO_3.

CHLORIDE OF SILICON.

Atomic or equivalent weight, assuming it to be represented by $SiCl_2$	126·3
Specific gravity	5·9

Preparation.—By transmitting a current of dry chlorine through a mixture of finely divided silicic acid and charcoal heated to redness in a porcelain tube. The silicic acid employed in this operation must have been prepared artificially, mere powdered flint or rock-crystal not answering well. Its intimate admixture with charcoal may be most conveniently effected as follows:—Mix intimately equal parts, by weight, of recently prepared silicic acid and lamp-black; make the whole into a stiff paste by incorporating with it a sufficient amount of any fixed oil; mould the result into pellets, and having imbedded the latter in a crucible, lute on a cover, and expose the crucible to a red heat. When the crucible has been removed from the furnace, and allowed to cool, the pellets are ready for treatment with chlorine, as directed. The resulting chloride of silicon must be collected in a receiver, maintained cool by a mixture of ice and salt.

Properties.—Chloride of silicon is a limpid transparent fluid, colourless when pure, having a density of 1·52, boiling at 138° Fah., and fuming when exposed to the air, on account of aqueous moisture present in the latter. When brought into contact with water, it is immediately decomposed, yielding hydrochloric and silicic acids, as already described.

CARBON.

Equivalent or atomic weight . . . . = 6.

Carbon is one of the most important of chemical elements. Whether we contemplate the widely different aspects it can assume when uncombined, or the wonderful facility of uniting with other bodies which it possesses, carbon offers pre-eminent claims to the attention of the chemist.

Although carbon, both in its simple, or uncombined state, and in combination, is found in the mineral kingdom, yet it is the element which, *par excellence*, may be regarded as belonging to organic nature. Hence by far the greater number of carbon compounds will come under the reader's notice under the head of organic chemistry; yet it must be understood that the limit separating inorganic from organic chemistry is purely conventional. Carbon, in its pure and crystalline state, is the well-known, though rare and costly, diamond. It also occurs native, and almost pure, as plumbago, graphite, or black-lead. Carbon, under every form of aggregation, is totally infusible at the highest known temperatures. Ignited in an atmosphere of oxygen, however, even the diamond burns, and so combustible is the porous carbon artificially produced, and known under the name of charcoal, that it constitutes an ordinary fuel. All the ordinary materials from the combustion of which we develop light and heat are, in point of fact, either carbon, or combinations of carbon with hydrogen; and in con-

nection with this fact should be mentioned the important characteristic that the result of the combustion of carbon is gaseous. Had that result been a solid, none of our ordinary materials of fuel could have been employed for this purpose.

It would be out of place in a treatise on chemistry to enter upon several details concerning the diamond, which derive their interest mainly from the adventitious and, to the chemist, the unimportant fact that the gem is so highly prized. It will suffice to mention that the gem crystallizes in forms belonging to the regular, or tessular, system; that it is the hardest substance known; and that all attempts at its artificial formation have been in vain. It is found in certain alluvial districts of India and Brazil, and is believed by many chemists to be a result of organic decomposition. The nature of this decomposition is still a mystery; but the experiment of converting the diamond into coke by igniting it intensely between two charcoal points transmitting voltaic electricity, seems to prove that elevated temperature can have had no part in its original formation.

Crystallized carbon is not only found naturally in the form of the diamond, but as a mineral species known by the appellation plumbagine; the crystals of this material, however, are not white and transparent, but black and opaque.

The specific gravity of carbon differs for each of its physical conditions. Thus, the specific gravity of the diamond is 3·50, whilst the specific gravity of plumbago is only 2·20, and of powdered coke from 1·60 to 2·00.

The conducting power of carbon for electricity not only varies for various physical aspects of the substance, but for modifications of the same aspect. Thus, although ordinary wood charcoal, prepared at no very high temperature, conducts electricity badly, charcoal, prepared at high temperatures, is a remarkably good conducting body.

Certain varieties of porous charcoal possess the remarkable property of absorbing large volumes of different gases, and also odorous miasmata; and certain varieties, especially those resulting from incineration of animal products, have the property of removing vegetable and animal colours. This latter property is taken advantage of very extensively in the prosecution of several manufactures on the large scale.

Carbon has a strong tendency to unite with oxygen, when exposed to high temperatures, in admixture with bodies containing the latter. Hence its great power as a reducing agent for converting metallic oxides into the respective metals—a process appropriately known by the term *reduction*.

Combinations of Carbon with Oxygen.—There are several combinations of carbon with oxygen, but of these only two properly belong to the department of inorganic chemistry. These are carbonic oxide and carbonic acid. Their composition is as follows:—

	Parts by weight.		Equivalents or atoms.	
	Carbon.	Oxygen.	Carbon.	Oxygen.
Carbonic oxide . .	6	8	1	1
Carbonic acid . .	6	16	1	2

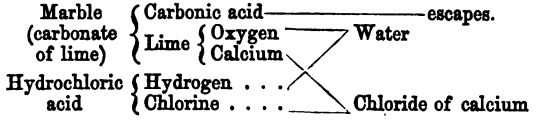
CARBONIC ACID.

Atomic or equivalent weight .	= 22
Atomic or equivalent size . . .	= □
Specific gravity . . .	= 1·529

History, Natural History, and Synonymes.—Carbonic acid was discovered by Dr. Black in 1757, and described by him as fixed air. He demonstrated the existence of carbonic acid in limestone, and carbonate of magnesia, and showed the gas to be formed as a consequence of respiration, fermentation, and combustion. Lavoisier was the first to demonstrate its composition synthetically by the now common operation of igniting charcoal in a jar of oxygen gas.

Preparation.—The most convenient method of preparing carbonic acid for experimental purposes consists in the decomposition of a carbonate by mixture with some acid capable of displacing the carbonic. In practice, marble broken into small pieces is the most convenient form of carbonate, and aqueous hydrochloric acid (spirit of salt) is the most eligible acid. As the application of heat is unnecessary in conducting this operation, the generating vessel may be a wide-mouthed bottle, to which a funnel apparatus and bent tube have been attached. It may be collected either over water, mercury, or by displacement. Water dissolves about its own volume of carbonic acid gas at ordinary temperatures and pressures; but this amount is not sufficiently great to interfere with the collection of carbonic acid over water.

The decomposition which ensues when carbonate of lime (marble) is brought into contact with hydrochloric acid is as follows:—



Or in symbolic notation it is thus represented:—

$$CaO_1CO_2 + HCl = CaCl + HO + CO_2.$$

Properties.—Carbonic acid, under ordinary temperatures and pressures, is a pungent, colourless, heavy gas; at 60° Fah., and under a pressure of 30 inches bar., 100 cubic inches weigh 50·03856 grains. Carbonic acid was amongst the first of gaseous bodies converted into the liquid condition, and furnished chemists with the first example of a gaseous body reduced to the state of solidity. At the temperature of 32° Fah. the liquefaction of carbonic acid may be accomplished under a pressure of 36 atmospheres; but if the temperature be reduced to 14° the same result may be accomplished by a pressure of 27 atmospheres. At the low temperature of — 22° Fah., producible by mixing together crystallized chloride of calcium and ice, its liquefaction may be accomplished at a pressure of 18 atmospheres. Liquid carbonic acid is a colourless liquid, which if cooled down to the very low temperature of about — 94° Fah. freezes.

Carbonic acid is soluble in water even at ordinary temperatures and pressures, conferring upon the liquid a brisk, agreeable taste. All effervescent alcoholic liquors hold carbonic acid in solution; so do ginger-beer and soda-water. Much of the so-called *soda-water* found in commerce is totally devoid of soda or other alkali, being

merely a solution of carbonic acid in water under pressure. A somewhat remarkable circumstance in relation to the quantity of carbonic acid capable of being absorbed by water is this:—Whatever be the density of the carbonic acid, water dissolves a volume of it nearly equal to its own.

Carbonic acid, in its gaseous or ordinary condition, is a heavy, irrespirable, incombustible gas, neither capable of supporting combustion nor the function of respiration. Both the gas and its aqueous solution redden litmus-paper feebly, thereby manifesting a characteristic of acidity. The acid properties, however, of carbonic acid are so weakly pronounced that its combinations with bases (carbonates) are decomposed by almost every other acid, carbonic acid being evolved. Carbonic acid, and its aqueous solution, are rapidly absorbed by the caustic alkalies and alkaline earths, a carbonate being generated in either case. Carbonates of alkalies are soluble, those of the earths insoluble. The white precipitate generated in solutions of lime or baryta (lime or baryta water), by the transmission of carbonic acid, or the addition of carbonic acid in solution, or a carbonate, is, when individualized by other necessary tests, a convenient means of indicating the presence of carbonic acid. Thus, if a gas or a solution yield a white precipitate with lime or baryta water, the precipitate *may* be a carbonate. If the precipitate dissolve in nitric or hydrochloric acid, evolving a gas which manifests the peculiar characteristics of carbonic acid gas, it *must* be a carbonate.

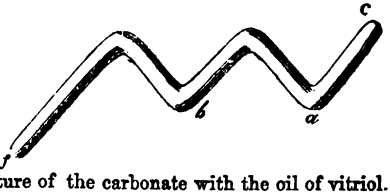
The functions of carbonic acid are very important in nature. It is always present in the atmosphere, though the quantity is variable, ranging from ·4 to ·6 per cent. Trivial though this amount may seem, it suffices to afford the necessary quantity of carbon to the whole vegetable creation. As regards the mineral kingdom, vast stores of carbonic acid are locked up in the form of carbonates, chiefly of lime. In some localities these carbonates are decomposed by natural causes, when carbonic acid of course escapes. Being heavier than the atmospheric air, carbonic acid may be poured from one vessel to another in the manner of a liquid; hence, if it happen to be liberated in a pit or valley, it lingers there, and may be recognised by its effects.

The celebrated Grotto del Cane, near Naples, owes its mephitic properties to carbonic acid thus collected; and the secret of its proving fatal to dogs, though failing to injure human beings, is easily explained. The Grotto del Cane is formed in such a manner, that it may be compared to a pitcher lying on its side, from which arrangement it follows that the accumulated gas can never rise sufficiently high to affect the breathing organs of a human being, though a small quadruped readily succumbs, because its mouth and nose are below the deadly level

Still more celebrated than the Grotto del Cane, but not so commonly associated with the true cause of danger, is the celebrated Poison Valley of Java, the deadly influence of which was attributed, by the early Dutch travellers, to the Upas tree. There are poisonous trees in Java termed Upas, and the concentrated Upas juice is sufficiently terrible; but the accounts once received as true, to the effect that only one tree of the kind grew in Java, that it exhaled a poisonous atmosphere fatal to all beings, animal and vegetable, within a radius of several miles, is a fable. The true state of the case is this:—There is in Java a valley about half-a-mile in diameter, and having very steep sides. This valley is charged with carbonic acid, evolved from natural fissures, and consequently represents the phenomena of the Grotto del Cane on a much larger scale.

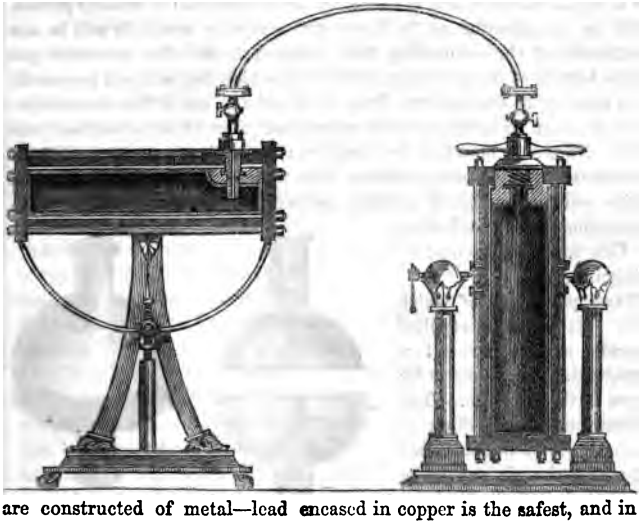
Carbonic acid, though filling an important part in the general economy of nature,

is not extensively employed for artificial purposes. Many of its salts, especially the carbonates of potash and soda, are largely used in the arts and manufactures; but they are invariably made by indirect processes not involving the primary employment of carbonic acid. Perhaps the most ingenious and refined application of carbonic acid is its employment for the generation of extreme degrees of cold. This is effected by the spontaneous evaporation of liquid carbonic acid, or a mixture of solid carbonic acid with ether. The liquefaction and solidification of carbonic acid have been already adverted to; the method now requires to be indicated by which the liquefaction and solidification in question are accomplished, both on the small and the large scale. On the small scale the liquefation of carbonic acid was first accomplished by Mr. Faraday, by exposing it to the pressure of its own elasticity. Into a tubular apparatus, bent as represented in the accompanying diagram, some oil of vitriol and bicarbonate of soda or potash are placed, the former deposited in the bend *b*, the latter in the bend *a*; lastly, the tube is carefully fused at *c*, *f*



especial care being taken to prevent admixture of the carbonate with the oil of vitriol. The glass being sealed and the apparatus well cooled, a certain inclination is given to the instrument, by which means the sulphuric acid and the bicarbonate are brought into contact. Decomposition of the bicarbonate ensues, carbonic acid is evolved, and the extremity, *f*, of the tube apparatus, being cooled by a mixture of ice and snow, liquid carbonic acid condenses.

The same general principle is adopted in the generation of large quantities of liquid carbonic acid, but the apparatus is necessarily modified. It consists of two separate vessels, the generator and the receiver, as represented in the accompanying diagram, in which the vertical cylinder represents the generator, the horizontal one the receiver. Both

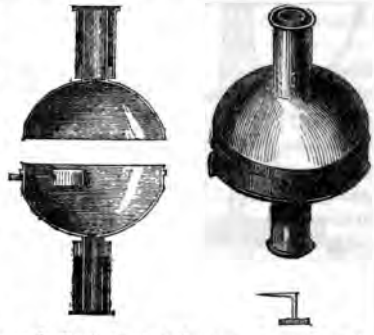


are constructed of metal—lead encased in copper is the safest, and in all respects the best, though cast-iron was employed originally. Without describing minutely the various parts of this apparatus, it will suffice to mention that the receiver is so constructed that a portion of bicarbonate of soda having been dissolved in water and poured

in, a slender cylinder of copper closed at one extremity, as represented below, may be hung within the cylindrical cavity. Supposing this disposition to have been made, it follows that no decomposition can ensue until the sulphuric acid and bicarbonate of soda have come into contact, which can be effected at any time, simply by inverting the generating cylinder; to facilitate which operation it is swung on a pivot. Let us assume then that, after securing a proper communication between the vertical, or generating vessel, and the horizontal, or receiving one, the former is inverted, causing the sulphuric acid within it to flow out and come into contact with the bicarbonate of soda. No sooner does this take place than decomposition of the bicarbonate results, carbonic acid is evolved, and, passing through the slender tube of communication into the horizontal receiver, is there condensed into the liquid form.

It remains now to be shown how carbonic acid from the liquid may be converted into the solid state. The student is desired to reflect that the act of evaporation always produces cold, and that, *ceteris paribus*, the degree of cold is commensurate with the rapidity of the evaporative process. Hence it is that the sensation of extreme cold is recognised when ether is poured upon the skin; and if that liquid be poured upon a thin glass bulb containing water, the water may be frozen. Hence it is, too, that water may be frozen by the cold resulting from its own evaporation under the exhausted receiver of an air-pump.

Bearing these facts in mind, it will readily be conceived that the evaporation of a liquid, so volatile as liquid carbonic acid—a liquid which can only be made to retain its condition of liquidity by artificial means—must be very rapid; and being so, that its evaporation must produce much cold. Such, indeed, is the fact: so intense is the cold that one portion of liquid carbonic acid is frozen by the evaporation of another portion. Returning now to an examination of the horizontal receiving vessel, it will be seen that the small extremity of the connecting tube between it and the generator goes almost down to the bottom of the receiving vessel, from which disposition it necessarily follows that if the receiver be disconnected from the generator, and if free communication be established between its cavity and the external air, a jet of liquid carbonic acid will be forced out. No sooner does this jet distribute itself than a portion of liquid carbonic acid becomes converted into a material like snow. M. Thilorier, who was the first to generate solid carbonic acid, not only devised the apparatus just described, but also a very ingenious box for collecting the solid acid. This box is represented by the subjoined diagrams.



It consists of two parts, one of which fits into the other. Each part is supplied with a hollow handle, and one part is furnished with a tangential jet, represent by the smallest figure in the diagram. The operation of the instrument is as follows:—Instead of allowing a jet of liquid carbonic acid to escape into the air and to be dispersed, it is caused to pass into the box through the tangential jet. Owing to this tangential direction, it is caused to circulate around the box. The fact need scarcely be indicated that no sooner does the

jet of carbonic acid enter the box than a portion freezes, owing to the cold produced by the rapid evaporation of the other portion. Hence, the box contains a mixture of gaseous and solid carbonic acid gas. But free communication is established between the inside of the box and the atmosphere without by means of the hollow handles; consequently all the gaseous portion readily escapes, whilst all the solid portion remains behind, and may be easily obtained by opening the box.

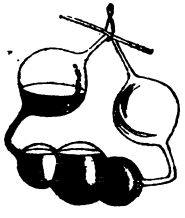
Solid carbonic acid, as thus produced, is capable of producing an intense degree of cold, as we shall presently discover; nevertheless, it may be handled with impunity—indeed, except it be forcibly squeezed, no particular sensation of coldness is remarked. This circumstance is easily accounted for. So great is the difference between the temperature of the carbonic acid and the temperature of the skin, that actual contact between the two does not occur—the solid carbonic acid being enveloped by an atmosphere of gas, and thus, like all gaseous bodies, having very imperfect powers of thermic conduction. Hence, when it is desired to apply the full cooling powers of carbonic acid, the substance has to be mixed with ether, in which it partially dissolves, forming a sort of paste. To touch this paste with the finger would be somewhat more dangerous than the act of touching a red-hot piece of iron; the application of extreme cold producing the same physiological effects as the application of extreme heat. By means of this ethereal paste the most surprising effects of cold may be developed. Quicksilver, when poured into it, causes a hissing noise, as when red-hot iron is plunged into water, and the metal is frozen at once. But, by peculiar management, the ethereal paste of carbonic acid may be caused to develop still lower degrees of cold. Its evaporation may be accelerated by placing it under an air-pump receiver, and creating a vacuum. In this way the astonishingly-low temperature of — 148° Fah.,—in other words, 148° below zero, or 180° below freezing point—has been produced.

Analytical Determination of Carbonic Acid.—The means of estimating carbonic acid qualitatively have already been mentioned; it remains, therefore, to indicate the method of its quantitative determination. This is usually accomplished by transmitting it through a solution of caustic potash, which absorbs it completely, the solution acquiring an increase of weight proportionate to the amount of carbonic acid absorbed. In this manner, the amount of carbonic acid contained in any gaseous mixture admits of being determined exactly, which is a matter of very great importance to the chemist, more especially when prosecuting organic analyses, in the course of which the total amount of carbon entering into the composition of a body is estimated, not as carbon, but as carbonic acid. We have already seen that charcoal (carbon), when burned in oxygen, yields an acid result (p. 284). If the experiment of charcoal combustion be now repeated, the gaseous result will be found to be endowed with the property of uniting with the lime of lime-water, rendering the fluid turbid, and also with caustic potash or soda.

These facts may be readily demonstrated by burning a piece of charcoal in two bottles, respectively filled with oxygen gas; when the charcoal has ceased burning, a lighted taper, if immersed in either of the bottles, will be extinguished, thus proving the existence of carbonic acid; but if a lump of quicklime, moistened with water, be thrown into one bottle, and a portion of liquor potassæ into the other, each bottle occluded with a glass plate (not the stopper, which would become fixed), and agitated for a few instants, all the previously-contained carbonic acid will be found, on opening the bottle, to have disappeared, as evidenced by a lighted taper no longer refusing to burn. Readily though carbonic acid is absorbed by solution of alkali, a perfectly

unexceptionable device for accomplishing this absorption is only a discovery of the last few years, and the merit of devising it belongs to Liebig.

It consists of a glass tube, bent, as represented in the following diagram, and expanded into five bulbs. The whole apparatus is constructed of very light glass, so that when partially filled with alkaline solution it will not be too heavy for weighing in a delicate chemical balance. The fact needs scarcely be indicated, that the bulb apparatus presents a current of carbonic acid transmitted through it to the alkaline solution, under conditions very favourable to the complete absorption of the gas: such is its intention. To convey an idea of the uses of this instrument, let us imagine the following case:—Assuming that the potash bulb apparatus, with its charge of alkaline liquid, weighs eight hundred grains, let us suppose a piece of charcoal to have been burned in contact with oxygen, converted into carbonic acid gas, and the latter passed *into* one extremity of our potash bulb apparatus; *through* the apparatus it will not go, inasmuch as the contained alkaline solution will absorb the gas. Under these circumstances the potash bulb will have increased in weight by a certain amount, corresponding with the weight of carbonic acid generated: supposing the piece of carbon burned to have weighed six grains, the weight of carbonic acid produced will be twenty-two grains, and the weight of the potash bulb, now charged with carbonic acid, will be 822 grains. Sometimes, in practice, the conversion of carbon into carbonic acid, preparatory to its estimation in the manner described, is effected by heating it in a tube, traversed by a current of oxygen gas; but, more frequently, the amount of oxygen necessary for combustion is yielded by some oxidising body. for this purpose the black oxide of copper is ordinarily employed. The manipulative details required in conducting this process belong to the department of organic chemistry.



CARBONIC OXIDE.

Equivalent or atomic weight . . . = 14

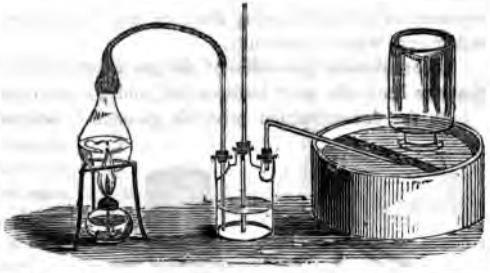
Equivalent or atomic volume . . . = $\boxed{}$

Sometimes a pale blue lambent flame may be observed burning on the surface of a charcoal fire; it results from the combustion of carbonic oxide gas, the nature of which may be half inferred from a consideration of the circumstances under which it occurs in the example before us.

Carbonic oxide may be regarded as the result of deoxidation of carbonic acid by some body having an affinity for oxygen. Carbon is a body of this kind; hence, when carbonic acid comes in contact with red-hot charcoal (carbon), one equivalent of oxygen is removed from every equivalent of carbonic acid, and carbonic oxide results. By far the most convenient method of generating this gas pure, however, is the following.

Preparation.—Oxalic acid, which properly belongs to the department of organic chemistry, may be regarded as consisting of one equivalent of carbonic acid, plus one equivalent of carbonic oxide. At least anhydrous oxalic acid has this composition—the acid which combines with oxide of silver, of lead, and certain other bases. Ordinary crystallized oxalic acid, however, contains three equivalents of water. Two of these three equivalents may be removed without destroying the constitution of the acid; but

without the third the acid cannot exist—it divides into carbonic oxide and carbonic acid. Now, oil of vitriol, as we have on many occasions recognised, has a powerful tendency to unite with water. By virtue of this tendency, when distilled with crystallized oxalic acid (oxalate of water, as we may with propriety term it), it decomposes that substance, appropriating all its water, and liberating carbonic oxide and carbonic acid gases mixed together. Now, alkalies absorb carbonic acid, but do not absorb carbonic oxide; therefore, on conducting the mixed gases into liquor potassæ, the only gas which bubbles through the latter is carbonic oxide. Hence the proper arrangement for procuring carbonic oxide by this process, is as represented above.



Properties.—Carbonic oxide is a colourless, inodorous gas, devoid of acid, and of basic properties. It does not render lime or baryta water turbid, in which respect it differs from carbonic acid. It has never been liquefied. It is very poisonous when taken into the lungs, and is not a supporter of combustion; but when ignited, it burns with a pale blue flame, the sole result of its combustion being carbonic acid. The specific gravity of carbonic oxide is ·9674.

SULPHUR WITH CARBON (SULPHIDE, OR SULPHURET OF CARBON).

One combination of sulphur with carbon is known to chemists. It is the bisulphuret, and composed, therefore, of one equivalent of carbon plus two of sulphur. Hence its atomic weight is 32 + 6, or 38.

Preparation.—By transmitting sulphur vapour over red-hot charcoal.

Properties.—A colourless liquor, possessing an extremely disagreeable odour, and having a specific gravity of 1·271 at 60° Fah.

CARBON AND NITROGEN (BICARBURET OF NITROGEN, OR CYANOGEN).

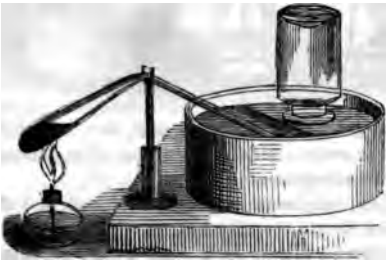
Equivalent or atomic weight . . .	= 26
Equivalent or atomic volume . . .	= [ ]
Specific gravity	= 1·86

General Remarks.—Cyanogen was discovered by M. Gay Lussac. It possesses great importance, both practical and theoretical; practical, on account of its being a constituent of hydrocyanic, or prussic acid, and a vast number of useful compound bodies; theoretical, as furnishing the most prominent example of a compound body acting like a simple one in chemical combinations. Thus, it combines with hydrogen, forming hydrocyanic, or prussic acid, the analogue of hydrochloric acid; with oxygen, to form cyanic acid, and in like manner for many other combinations. Perhaps cyanogen, on account of its numerous organic relations, belongs with most propriety to the domain of organic chemistry; nevertheless, its general characteristics so much resemble those of chlorine, iodine, bromine, and fluorine, that we will enter upon its consideration here.

Preparation.—Direct combination of carbon with nitrogen has never yet effected, hence an indirect process is requisite for generating cyanogen. This in process consists in heating cyanide, or cyanuret of mercury. A small bent tu represented by the following diagram, may be employed, and the gas may be col either over water or mercury.

If considerable quantities of the gas are required, it is hardly necessary to m that the bent tube must be discarded, and a small retort employed instead.

As the decomposition proceeds, gaseous cyanogen and metallic mercury w liberated; but there also remains retort a black material of precise same composition as cyanogen, which the denomination of par ogen is applied.



Properties.—Cyanogen is a col gas, possessing an odour somethi that of peach blossoms. It is co tible, and exceedingly poisonou all known gaseous bodies cyano one of the most easily conde By employing a pressure of 4 atmospheres it may be liquef ordinary temperatures; and it liquefies without pressure if cooled down to 4° Water dissolves 4 or 5 times its own volume of cyanogen gas, and alcol much as 20 or 25 volumes. Both alcoholic and aqueous solutions undergo d position by keeping; a brown powder being deposited, the nature of which h been determined.

CYANOGEN AND HYDROGEN (HYDROCYANIC, OR PRUSSIC ACID).

Equivalent or atomic weight . . .	=	27
Equivalent or atomic volume . . .	=	[ ][ ]
Specific gravity of vapour . . .	=	·947
Specific gravity of liquid	=	·697

Various processes have been devised for generating hydrocyanic, or prussic differing in their nature according to the strength of acid required.

ANHYDROUS HYDROCYANIC ACID.

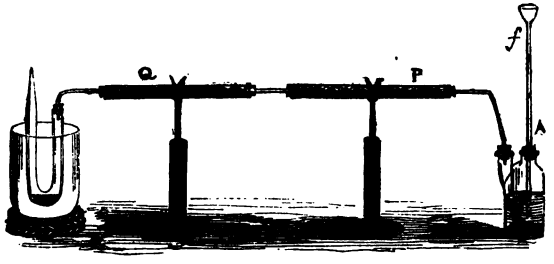
Preparation—Andydrous hydrocyanic acid may be prepared by transmitt current of hydrochloric acid gas over cyanide of mercury placed in a glass tub condensing in a U-tube, cooled by a mixture of ice and salt, the liberated hydro acid, in which case the decomposition is as follows:—

$$HgCy + HCl = HgCl + HCy.$$

But still better is it to substitute a current of hydrosulphuric acid gas for the h chloric. The arrangement of apparatus for conducting the operation is as follow

The bottle A contains fragments of sulphuret of iron, upon which dilute sul acid may be poured by means of the funnel *f*, and hydrosulphuric acid will, of c be liberated (page 349); but the gas is charged with aqueous vapour, from wh must be freed: this is accomplished by causing it to traverse some fragme

chloride of calcium contained in the tube P; passing on, it eventually comes in contact with crystals of cyanide of mercury contained in the tube Q, and no sooner does it touch them than decomposition ensues, sulphuret of mercury being formed, and hydrocyanic acid escaping into the cooled U-tube, where it condenses into the fluid condition. In order to obtain the hydrocyanic acid completely unmixed with hydrosulphuric acid, it is necessary to terminate the operation while yet a portion of the cyanide of mercury remains undecomposed. The progress of decomposition can be readily determined by noticing the colour of the materials in the tube—sulphuret of mercury is black, and cyanide of mercury white; moreover, the process of decomposition is regular, beginning at the extremity of the tube Q nearest to the generating bottle, and thence gradually proceeding to the farther extremity.

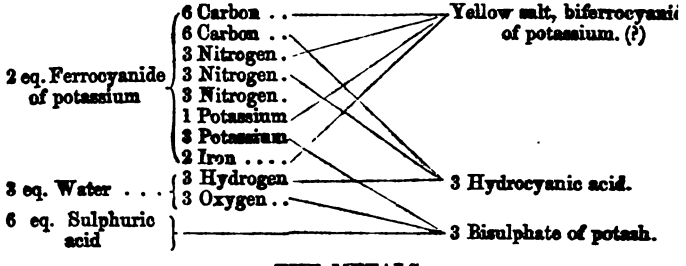


Properties.—Anhydrous hydrocyanic acid is a colourless liquid, and one of the most poisonous compounds known. A single drop placed on the tongue or in the eye of a strong dog, kills the animal instantaneously, and its vapour taken into the lungs is quite as deadly. For this reason the operation of preparing the anhydrous acid must be conducted with extreme care. Anhydrous hydrocyanic acid is exceedingly volatile; for this reason, when poured upon a flat surface, one part freezes by the cold resulting from the evaporation of the rest.

Dilute Hydrocyanic Acid.—Hydrocyanic acid dissolves in water in all proportions, and is frequently manufactured in the dilute state. That which is known in commerce as Scheele's strength is a five per cent. acid; but the dilute hydrocyanic acid of the London Pharmacœpia only contains two per cent. For preparing the acid on the large scale the following process may be adopted with advantage:—To 6 lbs. avoirdupois of powdered prussiate of potash (ferrocyanide of potassium) in a capacious retort add a mixture of 4½ lbs. oil of vitriol, and 12 pints of water. Distil by the heat of a sand-bath into 2 gallons of water, until the materials in the retort acquire the consistence of a thick paste. The resulting dilute acid will be stronger than acid of Scheele's strength (5 per cent.), but the determination of its exact strength requires an analytical process of the following kind:—Weigh off any convenient quantity of the acid—say 50 grains—and add solution of nitrate of silver until no further precipitation ensues. Collect the precipitate on a tared filter, wash it thoroughly dry, and weigh. The white precipitate is cyanide of silver, every 134 parts of which correspond with one equivalent, or 27 parts, of hydrocyanic acid; consequently it will be seen that, by dividing the weight of cyanide of silver produced by 5, the quotient indicates the quantity, within an unimportant fraction, of hydrocyanic acid present. As regards the greater number of solutions, specific gravity is correlative with strength; but dilute hydrocyanic acid furnishes an exception to the rule, inasmuch as the difference of its specific gravity for different strengths is only trifling. In reducing hydrocyanic acid of one strength to another specified strength, the following considerations

must be attended to. Suppose that we aim at the manufacture of a 5 per cen but having tested it by means of nitrate of silver, 50 grains yield 13 grains of cy silver. Now 13 divided by 5 give 5·2; hence the dilute acid has a strength of cent. But we desire to have an acid of exactly 5 per cent.; therefore we m follows:—5 per cent. is one-twentieth; hence, if we take twenty parts of 5 p acid, and extract the real acid from it, the latter will be found to have been i bination with 19 parts of water; hence, if we multiply the amount of real acid we get the number of parts by weight of water, which must be combined wi form an acid of 5 per cent. strength. Now $20 \times 5{\cdot}2 = 104$; hence every 1(of the acid of 5·2 per cent. must have water added to it until the total number by weight is 104. To every 100 parts by weight of acid of 5·2 per cent. st therefore, we must add 4 parts of water. Frequently in practice it is more con to measure than to weigh liquids, though weighing is always more correct. operation of measuring be applied to data relating to weight, allowance must b for the difference between the specific gravities of the liquids operated on. T the present case, dilute hydrocyanic acid having a strength of 5·2 per cent. p the specific gravity of ·995; that is to say, it is lighter than water in the ·995 to 1; hence the measure of a pound weight of water will not hold a pound of a liquid of ·995; but less than a pound in the ratio of $\frac{1}{\cdot 995}$ to 1, or 995 to hence, in order to make up the pound for every 1000 measures of water, we mus 1005 measures of a liquid having a specific gravity of ·995. Now 1005 is th as $\frac{1}{995}$; it is, in point of fact, the reciprocal of 995, or unity divided by 995 decimals 1005.

The decomposition which ensues in the preceding operation has been stu the late Mr. Everitt,* according to whom the following changes occur:—



THE METALS.

Characteristics of Metals.—Perfectly distinctive though the characteri metals on casual observation may seem, and which indeed is true so long as we our attention to those metals which ordinarily come under our notice, several bod known to chemists the classification of which is by no means easy; so thorou they unite the prominent characteristics of metallic with those of non-metallic Nearly all the arbitrary qualities which at various times have been associat metals, the progress of chemical discovery has in turn obliterated. At one time a lustrous appearance was thought to be necessarily characteristic of metals; but

* "Phil. Mag.," Feb. 1835.

quality many exceptions are known. Great specific gravity, again, was long considered to be the invariable concomitant of the metallic state; but the discovery of the alkaline radicals—potassium and sodium—universally accepted as metals, annihilated the dictum. Then, again, opacity was said to be an invariable quality of the metallic state; but gold-leaf may be beaten so thin as to admit the passage of light, not through little apertures in the thinly-hammered leaf, but through the substance of the metal. This is proved by the decomposition which white light undergoes in its transit. The light which passes through the gold-leaf is invariably green, notwithstanding that the original light might have been colourless. With the exception of the doubtful example of *ammonium*, metals have never been decomposed. The alchemists believed that metals were compound bodies, and might be mutually transformed amongst themselves—the common metals into silver and gold, and those too back again. The whole tendency of modern chemistry is at variance with this assumption.

As regards colour, metals present but little variety. Gold is the only yellow metal, copper and titanium are red, and all the rest are more or less white; the shade of whiteness varying from the pure dead white of silver to the bluish-gray of lead. With respect to the state of their physical aggregation, metals differ widely, as is evidenced by the different amount of malleability, tenacity, brittleness, hardness, and softness possessed by different metals. Of all metals, gold is the most malleable.

Silver, in this respect, comes next to gold; then copper, tin, and platinum. Iron, palladium, cadmium, nickel, lead, potassium, sodium, and mercury, when frozen, are all malleable. Zinc is brittle at some temperatures, malleable at others. The most brittle metals are arsenic and antimony.

The amount of ductility possessed by any metal is correlative with its tenacity or power of being drawn out into fine wire. It is a quality somewhat allied to malleability; however, the two are not identical, as the following arrangement, in which eight metals are arranged in the order of their tenacity, will prove:—

Iron	Gold
Copper	Zinc
Platinum	Tin
Silver	Lead

The tenacity of a wire is measured by the suspension of weights until the wire breaks. The weights are for each wire correlative with its tenacity.

The density, or specific gravity, of metals varies between wide limits; platinum being nearly twenty-one times heavier than water, potassium lighter than water in the ratio of 1 to ·865. The following table expresses the density, or specific gravity, of the metals:—

Specific Gravity of Metals. Temp. 60° Fah.

Platinum	20·98	Arsenic	5·88
Gold	19·26	Nickel	8·28
Tungsten	17·60	Iron	7·79
Mercury	13·57	Molybdenum	7·40
Palladium	11·30 to 11·8	Tin	7·29
Lead	11·35	Zinc	6·86 to 7·1
Silver	10·47	Manganese	6·85
Bismuth	9·82	Antimony	6·70
Uranium	9·00	Tellurium	6·11
Copper	8·89	Titanium	5·30
Cadmium	8·60	Sodium	·972
Cobalt	8·54	Potassium	·865

Fusibility of Metals.—Fusibility is a quality common most probably to metals. Arsenic, however, when heated at the ordinary atmospheric pressure chan from the solid to the vaporous condition, without passing through the intermedi state of liquidity. The temperature at which the fusion of metals occurs varies betw wide limits—from mercury, which is fluid at ordinary atmospheric temperatures, platinum and a few others, which are infusible at the highest furnace heats.

The following table indicates the fusion point of metals:—

		Fah.
Fusible below a red heat.	Mercury	— 39°
	Potassium	136°
	Sodium	190°
	Tin	442°
	Cadmium	about 442°
	Bismuth	497°
	Lead	412°
	Tellurium	rather less fusible than lea
	Arsenic	unknown.
	Zinc	
	Antimony	just below redness.
	Silver	1873°
	Copper	1996°
	Gold	2016°
	Cast iron	2786°
	Pure iron, Nickel, Cobalt, Manganese, Palladium	Fusible by the greatest heat of a wind furnace.
	Molybdenum, Uranium, Tungsten, Chromium	Imperfectly fusible in a wind furnace.
	Titanium, Cerium, Osmium, Iridium, Rhodium, Platinum, Columbium	Not fusible by the highest furnace heats: fus in the flame of hydro-oxygen blow-pipe.

Iron, platinum, and the alkaline metals acquire a pasty state before perfect fu owing to which property, two or more pieces may be hammered or pressed into This operation is termed *welding*, and in the case of iron and platinum it is turne practical account. Probably all metals would be volatilized if a sufficient amou heat could be applied. Some are easily volatilizable, and may, therefore, be distil mercury, arsenic, and tellurium are pre-eminent in this respect, both passing o vapour at temperatures below redness. Potassium, sodium, zinc, and cadmium only volatile when heated to redness.

Chemical Relations of Metals.—Although the physical properties of metals which have been described are important to the chemist, nevertheless their combining properties with which he is chiefly concerned. These I shall proceed to discuss.

Direct Combinations of the Metals with each other.—The greater number of m admit of being fused together into compound metallic masses, to which the general

alloy is applied, provided mercury do not form part of the combination, in which case the term *amalgam* is employed. Metals capable of being alloyed apparently unite in all proportions; nevertheless, a tendency to a definite atomic constitution is generally recognizable; and when the due atomic proportions are departed from, the resulting compound manifests indications of being a mere mixture.

Combinations of the Second Degree.—By the term metallic combinations of the second degree may be designated the results of the union of metals with non-metallic elements, such as oxygen, chlorine, sulphur, silenium, fluorine, &c., constituting oxides, chlorides or chlorurets, sulphides or sulphurets, selenides or seleniurets, fluorides or fluorurets, &c. Of these the combintions of metals with oxygen are the most numerous and important. The due understanding of chemical nomenclature, as at present followed, depends upon their full appreciation. It is, therefore, necessary to treat of them somewhat in detail.

DUALITY OR COMBINING TENDENCY OF ELECTRO-POSITIVE AND ELECTRO-NEGATIVE RADICALS.

The Acid and Basic Function.—The most superficial investigation of chemical phenomena will render evident the existence of two functions of matter chemically considered; functions in some way mutually opposed, but correlative, like the functions of northness and southness in magnetic, and positive and negative in electrical relations. To define these functions, to systematise them, and unravel the forces which determine them, are amongst the highest aims of philosophic chemistry, and have occupied, in succession, all the master-minds devoted to this science. In endeavouring to present the reader with an outline of this interesting part of chemistry, it will be well to adopt, provisionally, two theories, both of which have been proved incorrect, but which, nevertheless, have left such a deep impress on the structure of chemical philosophy—have so identified themselves with chemical expressions, and associated themselves with chemical reasonings, that the attempt to discard them altogether produces a chaotic array of facts, vague, and unsymmetrical. The hypotheses here adverted to are the electro-chemical theory of Davy, and the acid theory of Lavoisier.

During our investigation of the non-metallic bodies, we have seen that they are impelled by the force of affinity, or chemical attraction, to combine with each other; but we have hitherto taken no account of the difference of function as between two combining elements. In discussing the class of metallic bodies, this consideration will present itself emphatically. We shall, therefore, do well to acquire some consistent notions respecting it at once. Perhaps water furnishes the best starting-point for this train of inquiry. Water, the reader is aware, is the protoxide of hydrogen. It is a compound of oxygen with hydrogen; and if water be decomposed by voltaic electricity, its oxygen is always evolved at the positive pole, or extremity of the battery, its hydrogen being evolved at the other. Accepting as true the electro-chemical theory of Davy, oxygen goes to the positive pole, or end of the voltaic battery, because, *being itself negative*, it is attracted there, hydrogen going to the negative pole, or end, because of its own positive condition. Under the head of Electricity, it has been shown that the assumption of Davy is untenable. Neither oxygen nor hydrogen go to their respective poles because of their being attracted thither, and for this reason the term pole loses its former significance. The decomposition of water, however, by voltaic agency obviously points to the existence of a definite duality of force—a force the direction of which never changes; consequently, whatever be the inaccuracy of the

electro-chemical theory, the term electro-negative may be applied to oxygen, and electro-positive to hydrogen, with the practical advantage of facilitating the current of our reasoning. The terms *anion* and *cathion*, as I have before remarked (page 363), involve no hypothesis, and are, therefore, preferable to the terms electro-negative and electro-positive; they are scarcely so expressive, however, and have not displaced the terms electro-positive and electro-negative in practice.

But the duality of power which determines chemical combination assumes its most prominent form, and manifests its strongest energy, when compounds are concerned; hence, at a very early period of chemical investigation, arose the two expressions "acid" and "base," as indicative of these dualities. Of acid bodies we have already met with several examples during our consideration of the non-metallic elements; of bases, however, we have met with only one—*ammonia*. The metals will furnish a large accession to this class of bodies; in point of fact, the basic quality predominates throughout the whole metallic series.

If, instead of water, an aqueous solution, containing the elements represented in the subjoined table, be exposed to voltaic agency, decomposition again ensues, and the various elements resolve themselves into two groups, as represented by the brackets. From a casual examination of these groups, it will be seen that the first corresponds with sulphuric acid, the second with ammonia.

1 Sulphur 1 Oxygen 1 Oxygen 1 Oxygen	Go to positive terminal, or anode	1 Hydrogen 1 Hydrogen 1 Hydrogen 1 Nitrogen	Go to negative terminal, or cathode.

Accepting the evidence of this decomposition, we are driven to the necessity of concluding that the single elements entering into sulphate of ammonia do not unite into one mass, if the expression be permissible; but that they begin by associating themselves with other elements impressed with similar energy, and end by forming the compound dual arrangement—*sulphate of ammonia*.

By far the largest portion of bodies into which various elements enter, may be resolved into these compound dual groups by voltaic energy; and further examination will demonstrate these groups to possess many properties in common. For example, nearly all the groups which go to the positive pole or terminal (anode) of the voltaic arrangement are sour to the taste, and redden blue litmus paper; whilst all the groups which go to the negative pole, or terminal (cathode) of the arrangement, are totally devoid of sourness: on the contrary, many of them have a distinctive taste of their own, and which assumes its highest characteristic nature in the alkalies, potash and soda. None of them redden litmus-paper; but, on the contrary, change paper which has been thus reddened, back to its original blue colour; and, finally, they all possess a remarkable tendency to unite with bodies of the former dual group, generating resulting bodies to which the generic name *salt* is applied. It will be readily seen, therefore, that the general term *acid*, may be applied with great propriety to that class of compound bodies called—in respect of its voltaic relations—electro-negative, or *anions*, and base to electro-positives or *cathions*. Although, therefore, all salts are not necessarily compounds of an acid with a base, nevertheless every compound of an acid with a base is a salt (page 352).

I have already explained (page 352), that the first or original type of saline bodies was common salt, a body which was supposed to contain an oxygen acid and a base;

but which is now demonstrated to contain chlorine and sodium merely. It has been also remarked that the constitution of sea-salt, and other bodies of the so-called hydracid or haloid (page 352) group, is irreconcilable with the theory of oxygen acid salts, and that the tendency of modern chemistry is to elevate the formerly exceptional haloid constitution into the type, and refer all salts to that standard. But the reader of the preceding few pages may ask how are chemists to make this theory accommodate itself to facts as they are? What is the evidence to warrant our arriving at the startling conclusion that the compound termed sulphate of ammonia is *not* a compound of sulphuric acid and ammonia? If we add sulphuric acid to a solution of ammonia, do not the two combine, and do we not get sulphate of ammonia on evaporation? Furthermore, have we not seen that on decomposing sulphate of ammonia by voltaic electricity, we actually separate the sulphate of ammonia into its two constituents—sulphuric acid and ammonia? Specious though this reasoning may appear, it testifies nothing in favour of the existence of the so-called compound of sulphuric acid with ammonia.

Glancing at the composition of this salt, the first point that strikes us is the existence of one atom of water. Without water, sulphate of ammonia cannot exist. So much, then, as regards the synthetic formation of the salt: now a few words concerning the phenomena of its voltaic decomposition. Although the results of this decomposition are sulphuric acid on one side, and ammonia on the other, yet one fact has been overlooked. Simultaneously with the decomposition of sulphate of ammonia there is decomposition of water, hydrogen being evolved at the cathode or negative pole, and oxygen at the anode or positive. Having thus investigated the supposed evidence in favour of the existence of sulphate of ammonia as an actual compound of sulphuric acid and ammonia, we find the tendency of this evidence to be in the opposite direction. We are almost constrained, therefore, to believe in the existence of ammonium HN_4, and a combining group of SO_4; and this admitted, we establish a parallelism between oxyacid and haloid salts; or rather we abolish the speciality of the former. This is called the binary or the hydrogen theory of salts. The predominant idea on which it is based is the recognition of the quasi-metallic property of hydrogen, a property in virtue of which it can replace a metal in combination. According to this view, hydrated sulphuric acid will be composed of hydrogen plus the radical SO_4, and for which the names *sulphatoxygen* and *sulphoxion* have been proposed; thus, monohydrate of sulphuric acid, according to this view, is sulphatoxide of hydrogen, and sulphate of ammonia, with one atom of water, sulphatoxide of ammonium. In like manner, we should have sulphatoxide of barium instead of sulphate of baryta, and so on for other bases.

Objections to the Binary Theory.—Various objections have been adduced to the theory in question. The principal is the necessity which would arise for assuming the existence of numerous compound radicals which had never been obtained. But this objection applies to many substances recognised by our present nomenclature. Neither oxalic acid nor acetic acid has been obtained deprived of water, or at least the elements of water; and, a few years since, nitric acid belonged to the same category. The real objection to the binary or hydrogen theory is practical, not theoretical. So firmly has the nomenclature of Lavoisier established itself, and so accordant is it with our ordinary appreciations, that the abolition of this nomenclature in favour of any other, however philosophically appropriate, would be attended with enormous difficulties.

Advantages of the Hydrogen or Binary Theory of Salts.—(1). It reduces all saline bodies to one category, whereas the old theory necessitates several.

(2). It furnishes an intelligible reason for the remarkable law in the constitution of neutral or perfect salts, that whatever number of atoms of oxygen a base contains, a salt of that base must have an equal number of atoms of acid. This law is illustrated by the appended general formulæ of neutral sulphates.

As consisting of oxide and acid.	As consisting of metal and salt radical.		
$MO + SO_3$ . .	$M + SO_4$	Example:	Sulphate of soda.
$M_2O + SO_3$ . .	$M + SO_4$	„	Sulphate of suboxide of mercury.
$MO_2 + 2SO_3$ . .	$M + 2SO_4$	„	Suphate of peroxide of mercury.
$M_2O_3 + 3SO_3$ . .	$M_2 + 3SO_4$	„	Sulphate of peroxide of iron.

(3). It accords better than the old theory with the results of voltaic decomposition.

Neutral, Super, and Sub Salts.—The term *neutral salt* employed above renders an explanation of that term necessary, also the expressions super and sub salt necessary. Blue litmus-paper, or tincture of litmus, is, as we have seen, a test of acidity, nearly all soluble acids changing the blue to red. If, then, on testing the solution of a salt, it is found to turn blue litmus-paper red, the inference will be, according to the evidence of the test before us, that the salt in question contains an excess of acid; according, therefore, to the evidence before us, it may be said to be a *super salt*. In like manner, if a salt possesses the opposite reaction, changing reddened litmus-paper to its original blue condition, and affecting turmeric paper brown, then, according to the evidence before us, the base may be said to predominate; and, finally, if a salt neither affect litmus nor turmeric paper, it may be said, according to the evidence thus deduced, to be neutral.

The two expressions, *super* and *sub*, are now seldom used, except when the atomic composition of a salt is unknown, though the excess of base or of acid, as the case may be, has been clearly made out. Litmus and turmeric papers are found to be fallacious as indicative of excess of base and acid in saline bodies. A neutral salt is now considered to be a compound made up of a single atom of acid, combined with a single atom of base. The class of subsalts is now generally termed basic salts, because the base predominates; and if the number of atoms of a base entering into the constitution of a basic salt have to be indicated, this is effected by employment of the Greek numerals *dis*, *tris*, *tetrakis*, *pente*, &c.; conversely, the number of atoms of acid entering into the composition of an acid salt is now expressed by the Latin numerals *bi*, *tri*, &c.

KALEGENOUS METALS—POTASSIUM.

Equivalent or atomic weight . . . 39·2.

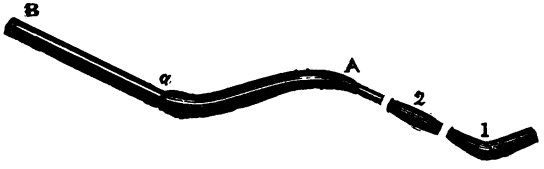
General Remarks.—Potassium was discovered by Sir H. Davy. It never occurs native or pure, on account of its great tendency to unite with other bodies, especially oxygen. Its compounds are very extensively diffused, both in the inorganic and the organic kingdoms. Many crystallized rocks contain potash (oxide of potassium) united with silicic acid; potash also enters into the composition of soils; but it is in the constituents of animal and vegetable beings that the most extensive diffusion of potassium compounds is recognised. All the potash which under various guises finds its way into commerce is, in point of fact, derived from the ashes of land vegetables.

Preparation.—(1.) Potassium was originally developed by transmitting a current of voltaic electricity through hydrate of potash (fused potash), slightly moistened, in order to increase its conducting power. Under these circumstances, water and potash

(oxide of potassium) were simultaneously decomposed, hydrogen and potassium being liberated at the negative pole or extremity (*cathode*) of the battery, and oxygen at the positive (*anode*).

(2.) The preceding operation yields potassium in small quantities only; to procure it in bulk the following process was next devised:—

An iron tube (gun-barrel or piece of gas-pipe), AB, having been bent as represented in the appended sketch, is charged with iron turnings from A to *a*, and with fused potash from *a* to B; afterwards, the portion of the tube from A to *a* is covered with a lute of refractory clay, that it may withstand the high furnace-heat to which it will be next exposed. The parts 1 2, disjoined from the main tube in the sketch, are for the purpose of enabling the tubular channel to be cleared, when necessary, from impediments.



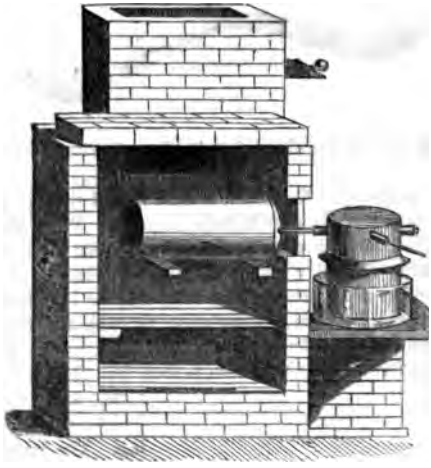
The tube having been charged and prepared as described, is next passed through a furnace from A to *a*, the remaining portion, from *a* to B, being exposed. When the furnace heat has been well raised, and the luted portion of the tube has been brought to a white heat, a wire basket, containing ignited charcoal, is hung underneath the tube from *a* to B, in order that the hydrate of potash (potassa fusa) may be liquefied. No sooner is this accomplished, that the fused material, percolating through the iron fragments extending from *a* to A, is decomposed—the oxygen of the fused potash, as also the oxygen of its water of combination, uniting with iron to form iron and potassium, and the hydrogen escaping. The latter passes into the air, and the former remains in the receiving vessel, *o*, containing naphtha, a liquid which, not having any oxygen in its composition, is unable to convert potassium into potash.

One portion of this apparatus yet remains to be described; it is the tubular appendix, *t*, which dips below the surface of mercury in a glass. The function of this appendage is as follows:—Occasionally the ignition-tube, notwithstand-

ing all the operator's care, becomes clogged, of which it is desirable that some indication should be recognizable, otherwise the tube might burst, and a severe accident be the consequence. The appendage *t*, with its associated mercury, at once supplies the indication of stoppage, and obviates danger, allowing any vaporous matter to escape, but preventing the access of atmospheric air.

(3.) By far the most eligible process for obtaining potassium in large quantities is by distilling a mixture of carbonate of potash and charcoal (carbon). The operation is usually conducted by means of a wrought-iron bottle coated with luting—a quicksilver bottle, such as was directed to be employed in the manufacture of oxygen gas, answers the purpose well. It is arranged horizontally in a furnace, as represented below.

During the process of potassium manufacture by distilling a mixture of carbonate of potash and charcoal, two peculiar salts of potash are formed, namely, the croconate, and rhodizonate of potash. Potassium, if required in a state of absolute purity, must be re-distilled in an iron retort containing naphtha.



Properties.—A white metal, having a yellowish tint, something like that of silver. At ordinary atmospheric temperatures it is soft, and two pieces may be readily pressed (welded) into one (page 396). When cooled down to 32° Fah., it is crystalline, and brittle. Its fusing point is 150°, and at 150° it passes into vapour, and may be distilled. In an atmosphere of hydrogen or nitrogen gas, potassium retains its metallic lustre, but it cannot long be exposed to the air without becoming incrusted with a pulverulent layer of oxide (potash). The tendency of potassium to unite with oxygen is very strong; it must, therefore, be preserved in naphtha, a fluid which contains no oxygen, or else in an atmosphere of non-oxygenous gas, such as nitrogen or hydrogen. When thrown upon the surface of water, on which it floats, or ice, it presents the phenomenon, extraordinary under the circumstances, of combustion; potash being formed and retained in solution by the water, and hydrogen evolved. The specific gravity of potassium is only ·865.

Compounds of Potassium with Oxygen.—There are two compounds of potassium with oxygen: the protoxide (potash, sometimes called potass or potassa), and the peroxide.

Protoxide (potash) KO.

Preparation.—Absolutely pure protoxide of potassium, or potash, is obtained with difficulty, though its monohydrate, fused potash, can be prepared with ease. When potassium is burned in a current of perfectly dry oxygen gas, it is not the protoxide (potash) or KO which results, but the peroxide or KO_3. If, however, twice the weight of potassium already held by this compound be mixed with it, and the whole heated in

a current of nitrogen gas, a compound made up of equal equivalents of oxygen and potassium results. This is the protoxide of potassium, or potash. When this oxide is dissolved in water, an ordinary aqueous solution of potash is obtained; but no known amount of heat can drive off the whole of the water, one atom for each atom of potash obstinately remaining, and constituting the monohydrate of potash, or ordinary potassa fusa. The two oxides of potassium differ widely as to their importance: one, the peroxide, is a mere chemical curiosity, applied to no useful purpose whatever; the other, *potash*, being a powerful base, and entering with acids into innumerable combinations.

The description of potassium and its oxides just given is strictly accordant with a synthetical examination of these bodies; but, practically, the order of producing them must necessarily be reversed, inasmuch as potassium does not naturally occur. The practical order of production is as follows:—In the first place, land plants—the source of potash—contain that alkali in combination with numerous vegetable acids. When these land plants are burned, the vegetable salts of potash are decomposed, being changed into carbonates. These carbonates are obtained by lixiviation of the vegetable ashes, filtration of the lixiviated matter, and evaporation. The result is carbonate of potash, contaminated with various impurities, most of which can be removed by re-solution, filtration, and evaporation.

Pure carbonate of potash being thus obtained, it is dissolved in water, mixed with quicklime, boiled, and filtered. The result is a solution of potash, or rather hydrate of potash in water. The decomposing agency of lime is simply to this effect:—It combines with carbonic acid, and forms carbonate of lime, which precipitates, leaving the solution of hydrate of potash alone. This solution may be freed from the carbonate of lime either by deposition or by filtration; if the whole of the carbonic acid has been removed, the solution will not effervesce on the addition of hydrochloric acid. The next operation consists in driving off as much of the water as possible; and this is effected by evaporation in a vessel of clean iron, or, still better, of silver. Proceeding thus with the evaporative process until its furthest limits are reached, a solid matter is obtained, which no further degree of heat can deprive of water, but which fuses, and may be cast into moulds. This material is the monohydrate of potash, and it is from this that potassium was originally prepared by voltaic agency. The second hydrate of potash is a crystalline compound, which forms, under some circumstances, in aqueous solutions of the monohydrate of potash, but which is applied to no useful purpose.

Monohydrate of potash has an extreme tendency to unite with water; a portion of it if exposed to the atmospere, even in the hottest weather, absorbs aqueous vapour, and changes to a syrupy liquid. It also absorbs carbonic acid, and is frequently employed for this purpose in many chemical operations. Hydrate of potash, when cast into the form of sticks, is employed by surgeons as a powerful caustic.

Few potash combinations are soluble in alcohol, but monohydrate of potash is an exception to the rule; it dissolves in alcohol readily, and by taking advantage of this property, it may be separated from carbonate of potash and many other impurities.

Inasmuch as the specific gravity of a solution of hydrate of potash increases with the amount of hydrate present, the strength of a solution of this kind will be proportionate with the quantity of hydrate present. The appended table indicates the relation between the two.

Density.	Per centage of real Alkali.	Density.	Per centage of real Alkali.
1·68	51·2	1·33	26·3
1·60	46·7	1·28	23·4
1·52	42·9	1·23	19·5
1·47	39·6	1·19	16·2
1·44	36·8	1·15	13·0
1·42	34·4	1·11	9·5
1·39	32·4	1·06	4·7
1·36	29·4		

CARBONATES.

Salts of Potash.—There are, at least, three carbonates of potash, probably more. They are the mono-carbonate, the bi-carbonate, and the sesqui-carbonate. The names indicative of the two former require no explanatory comment; the latter is so called from the Latin expression sesqui, one and a-half, because its composition accords with the symbol $KO\ 1\frac{1}{2}CO_2$, or, what amounts to the same, $2KO\ 3CO_2$.

Neutral, or Monocarbonate of Potash, $KO, CO_2\ 2HO$.—This salt is prepared in large quantities by lixiviating the ashes of land plants, as already described. In its impure condition it is termed crude potash; but when a little further purified the name pearlash is given to it. Absolutely pure carbonate of potash, however, is best prepared by igniting in a platinum or silver crucible pure bitartrate, or binoxalate of potash.

Bicarbonate and Sesquicarbonate of Potash, $KO, CO_2 + HO, CO_2$, are both prepared by transmitting a stream of carbonic acid through a solution of monocarbonate of potash.

Nitrate of Potash (Nitre or Saltpetre), KO, NO_5.—Next to the carbonates, this is, perhaps, the most important of all potash salts. It is used in the manufacture of nitric acid, and of gunpowder; it also is employed in numerous operations of chemistry, metallurgy, and the manufacturing arts.

Nitre occurs as a natural product in many parts of the world; it may be also generated artificially. We obtain all our nitre from India, where it occurs as a natural efflorescence on the ground in certain localities. Other nations, less favoured than ourselves in this respect, produce their nitre by an operation which will presently be described. Nitre, as it is imported from India, contains many impurities, from which it has to be separated before employment in the gunpowder manufacture, the manufacture of nitric acid, and most other purposes. Mechanical impurities may be obviously separated by solution and filtration. Lime is separated by the addition of carbonate of potash, which throws down carbonate of lime, and common salt is separated by frequent re-crystallizations. Crystals of nitrate of potash are anhydrous; their form is that of six-sided prisms, with dihedral summits.

An aqueous solution of nitre neither acts on litmus nor turmeric paper. It is soluble in seven times its own weight of water at 60° Fah., and in its own weight of boiling water. At a heat somewhat below redness it melts, and if the heat be pushed farther it is decomposed, yielding oxygen, binoxide of nitrogen, and many complex products.

The chemical agency of nitrate of potash has reference to the large amount of oxygen which it contains (six atoms), and the facility with which the latter is yielded up to deoxidising bodies. In many cases the act of imparting oxygen is attended with

combustion, as, for instance, when nitre is projected on red-hot coals. The phenomenon in question is termed deflagration. The theory of gunpowder as an explosive agent is explicable by a consideration of these facts: gunpowder is a mechanical mixture of nitre with sulphur and charcoal in different proportions, according as the result may be desired more or less strong for its various purposes. The results of the combustion of gunpowder vary for different specimens. In general terms, they may be said to consist of sulphuret of potassium, solid, and carbonic oxide, carbonic acid, nitrogen, and binoxide of nitrogen, gaseous. Great pain is taken to obtain nitre in the state of absolute purity before employing it as an ingredient of gunpowder. The most injurious contamination that it can contain is common salt, a body which not only absorbs hygrometric moisture, and thus tends to wet the gunpowder, but which, by taking no part in combustion, weakens the explosive violence. If the filtrate or filtered liquor from gunpowder, which has been rubbed up with water, yield with nitrate of silver solution a white precipitate soluble in ammonia, but insoluble in nitric acid, the presence of chlorine is demonstrated, and the existence in it of common salt may be inferred.

Artificial Production of Nitre.—If the floor of stables, the droppings of dove-cots, or similar materials rich in animal matters, be exposed to the air, the nitrogenous matters which they contain in the form of ammoniacal salts absorb oxygen in the requisite proportions to form nitrate of ammonia, which, by the addition of carbonate of potash, becomes changed into nitrate of potash. If carbonate of lime be present in the animal refuse, nitrate of lime is formed simultaneously with nitrate of ammonia, and is in like manner decomposed by the addition of carbonate of potash. The method of generating nitre artificially was discovered in France; the process is still carried on there, as well as in many other continental nations. In Sweden, each farmer pays a nitre tax in kind, not being allowed by his laws to compound for it by money.

Sulphate of Potash, KO, SO_3.—This salt may be made directly by the addition of sulphuric acid to hydrate of potash or carbonate of potash in single atomic proportions, subsequently evaporating the residue until crystals form; but it occurs collaterally in several chemical operations. Thus, for instance, when nitric acid is prepared by distilling nitre with oil of vitriol, decomposition ensues, nitric acid being evolved, and sulphuric acid formed. Sulphate of potash is soluble in ten parts of cold water; boiling water, however, absorbs a much larger quantity. Its solution does not affect test paper. Sulphate of potash is anhydrous, and quite insoluble in alcohol.

Bisulphate of Potash, $KO, SO_3 + HOSO_3$.—When the preceding salt is mixed with a sufficient amount of oil of vitriol to furnish a second equivalent of sulphuric acid, the result evaporated to dryness, fused in a platinum vessel, and finally re-evaporated, crystals of bisulphate of potash are formed. They are flattened rhombic prisms, much more soluble in water than the preceding salt. There is also an anhydrous modification of sulphate of potash formed by dissolving equal weights of the mono, or neutral sulphate, and oil of vitriol in a little warm water, and retaining the mixture cool until crystals form. If the crystals of this salt be allowed to remain for some days in the original solution, or if a larger quantity of water be added, they disappear, and the ordinary hydrated bisulphate results. A sesquisulphate of potash, $2KO,SO_3 + HO,SO_3$, has also been described by Mr. Phillips. He obtained it from the nitric acid residues; but M. Jacquelin has been unable to generate it.

Chlorate of Potash.—The general characteristics of this salt have already been described (page 362). It is made as follows:—A saturated warm solution of carbonate of

potash in water being prepared, chlorine gas is passed into it until no more is di The solution is next evaporated until a film appears, and set aside to cry Chlorate of potash, slightly contaminated with chloride of potassium, deposits. the latter it may be separated by two or three solutions and re-crystallisati the mother-liquor from which this crop of chlorate of potash has deposited be rated still more, a further crop of chlorate of potash, still more impure than t may be obtained. Finally, still further evaporation determines the forms crystals of chloride of potassium almost pure. Chlorate of potash crystallise anhydrous, tubular forms; they are soluble in about twenty parts of cold, an two of boiling water. The general analogy between chlorate, nitrate, iodat bromate of potash, has been indicated at page 317. Several attempts were ma former period, to substitute chlorate of potash for nitre in the manufacture o powder; the resulting compound, however, is far too dangerous for practice—it explodes on percussion, whilst gunpowder does not usually explode, except actually applied.

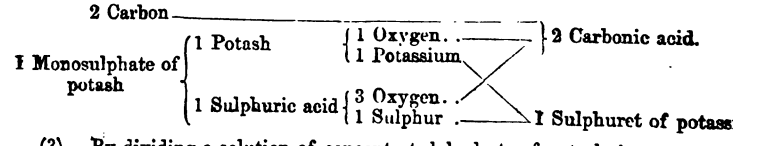
Perchlorate of Potash, KO, ClO.—Under the head of *perchloric acid*, at page 3 process for manufacturing this salt has already been described. It is characteri a degree of insolubility for a potash salt, each part requiring no less than fif parts of cold water for solution; boiling water, however, takes it up more r By the application of sufficient heat, perchlorate of potash is decomposed into o and chloride of potassium: the results of decomposition, therefore, are precisely i in kind to those of chlorate of potash, and only differ in the relative amo materials yielded from a given weight of original salt.

Sulphurets or Sulphides of Potassium.—When sulphur is fused with either hyd carbonate of potash, decomposition ensues, and a mixture of several compound merly believed to be combinations of sulphur with potash, results. These bod not compounds of sulphur with potash, but of sulphur with *potassium*; hence th sulphuret, or sulphide of potassium, correctly expresses their state of ch constitution.

MONOSULPHURET OF POTASSIUM.—KS.

Preparation.—(1). By fusing together single atomic proportions of potassiu sulphur.

(2). By mixing the mono, or neutral, sulphate of potash with charcoal p and heating the mixture to redness in a closed vessel. The theory of this dec sition is simple, and, at the same time, very interesting. Formerly, the opinic entertained that when sulphur was fused with hydrate of potash, or carbonate o alkali, a direct combination of sulphur with potash resulted. But the process consideration demonstrates the incorrectness of this opinion, for the monosulphu least, the decomposition being of the following kind:—



(3). By dividing a solution of concentrated hydrate of potash into two po saturating one with hydrosulphuric acid, then mixing it with the second portion finally, evaporating, and fusing, the whole.

Properties. - A red crystalline mass, soluble in water and alcohol, easily decomposed by acids, hydrosulphuric acid being evolved. In the same sense that we apply the theory of oxygen acids and bases, and say that ordinary salts are composed of acid oxides, united with basic oxides, so may we extend the expression to include acid sulphurets with basic sulphurets. Berzelius devoted much attention to this class of bodies, which he termed sulphur salts. Adopting this view, monosulphuret of potassium must be designated a very powerful base. It unites with various sulphurets, performing the function of acids, and generates well-defined crystalline compounds. The acid sulphurets particularly conspicuous in this respect are those of carbon, arsenic, and hydrogen (hydrosulphuric acid). If the monosulphuret of potassium be heated with a further quantity of sulphur, one or both of the higher sulphurets will result, according to the relative amount of sulphur and monosulphuret taking part in the decomposition.

Whatever be the relative amount of monosulphuret and sulphur, a portion either of hyposulphite of potash, or sulphate of that base, will also be formed simultaneously with the higher sulphurets.

SODIUM.

Equivalent or atomic weight . . . . 23.

General Remarks.—Sodium exists in the mineral, the animal, and the vegetable kingdom of nature; but never uncombined. The plants which contain this metal in any considerable abundance are either seaweeds, or certain vegetables which grow in the vicinity of the sea; of these, the barilla plant (*salsola soda*) is the chief. Sodium, as a constituent of the vegetable kingdom of nature, exists in the form of various salts of soda, having an organic acid; hence, when these salts are incinerated by burning the plants containing them, the soda is finally obtained in the state of carbonates. A fuller description of the carbonates of this alkali will be given hereafter.

As a constituent of the mineral kingdom, sodium is found in combination with silicic acid, constituting silicate of soda, a material which enters into the composition of various rocks. These mineral formations are very widely disseminated; but the sodium which they contain is nowhere found sufficiently localised to furnish a profitable source of sodium in any form of combination. Far otherwise is it with sodium in union with chlorine (chloride of sodium), or common salt. Not only does this compound exist to an enormous extent in the ocean, but in many parts of the world it forms subterraneous masses of rock-salt, obtainable, like other minerals, by the operation of mining.

Preparation.—Exactly like that of potassium, with the obvious substitution of carbonate of soda for carbonate of potash.

Properties.—In all its physical and chemical qualities, sodium bears a striking resemblance to potassium. It is not so blue as the latter, however, having more the colour of silver. It does not usually burn when thrown upon the surface of water, whereas, under this treatment, potassium never fails to burn. Its specific gravity is greater than that of potassium, being about 0 97, and it is volatilized at a somewhat lower temperature than that metal.

Compounds of Sodium with Oxygen.—There are two oxides of sodium,—the protoxide and the peroxide. The protoxide of soda is a compound of great practical importance; the other is a mere chemical curiosity.

Hydrates of Soda.—Probably, there are several hydrates of soda, but the only one

possessing any importance is the solid mass resulting from the evaporation, and subsequent fusion, of caustic liquor of soda. The process of making this caustic liquor is so completely analogous with that already detailed for making caustic liquor of potash, that further description is unnecessary. The fused hydrate of soda is the monohydrate, composed of one equivalent of soda and one of water; symbolically, therefore, it is represented by NaO, HO.

Sulphates of Soda.—There are several sulphates of soda, the most important of them being the neutral sulphate, containing ten atoms of water of crystallization (Glauber's salt) and the bisulphate. Neutral sulphate of soda may be prepared by dissolving forty-five parts of carbonate of soda in water, adding forty-nine parts of strong oil of vitriol (the monohydrate of sulphuric acid), and evaporating at a temperature below 68° Fah. This salt is much employed as a cattle medicine, and occasionally in the human materia medica. When exposed to air, its crystals effloresce, by losing their water of crystallization. On applying heat to the crystallized sulphate of soda with ten equivalents of water, they undergo the aqueous fusion, evolve water, and eventually deposit crystals of the anhydrous sulphate.

The act of dissolving Glauber's salt in water reveals some curious phenomena. Water at 32° only dissolves about five parts; but the amount capable of being dissolved increases rapidly up to 91·4, at which the maximum is attained. Beyond this the solubility again diminishes with the temperature. In addition to the sulphates of soda already detailed, there are others, but we need not occupy ourselves with them here. They may all be formed indirectly by decomposing chloride of sodium (common salt) with sulphuric acid, an operation had recourse to, as the student will remember, in the process of manufacturing hydrochloric acid. Anhydrous sulphate of soda may be fused alone without change; but if it be intimately mixed with carbonaceous matter and carbonate of lime, it is decomposed, the precise nature of the decomposition varying with the relative amount of materials employed. When the proportions consist of two equivalents of sulphate of soda, three of carbonate of lime, and nine of carbon, the final solid result is a mixture of insoluble oxysulphide of lime and carbonate of soda: of these the former is insoluble (the latter soluble) in water, and may be therefore washed out and crystallized. This is the theory of the celebrated process of Leblanc for preparing carbonate of soda from sea-salt.

The decomposition which takes place is represented by the following equation:—

$$2(NaO,SO_3) + 3(CaO,CO_2) + 9C = 2(NaO,CO_2) + 2(CaSCaO) + 10\ CO.$$

Sulphites of Soda.—Two compounds of sulphurous acid with soda are known—the *monosulphite* and the *bisulphite.*

Bisulphite of Soda.—Numerically considered, the monosulphite of soda should come first in our description, but certain practical reasons suggest a departure from this scheme.

Preparation.—When a current of sulphurous acid is transmitted through a mass of crystals of ordinary carbonate of soda, the following changes take place:—Firstly, a portion of sulphurous acid combines with a sufficient quantity of soda to form monosulphite, carbonic acid being liberated. The carbonic acid does not escape, however: it is immediately laid hold of by a portion of yet undecomposed carbonate, and bicarbonate of potash is the result. Still proceeding with the operation, the whole of the bicarbonate of soda becomes, in its turn, decomposed, and the monosulphite is gradually changed into the bisulphite of soda, which precipitates in small crystalline granules,

the deposition of which may be facilitated by the addition of alcohol to the solution. When bisulphite of soda is heated, sulphurous acid and sulphur are evolved, and sulphate of soda remains, a decomposition which is expressed by the appended scheme.

2 equiv. of bisulphite of soda	1 Sulphurous acid (escapes)			
	1 Sulphurous acid	1 Sulphur (escapes)		
		1 Oxygen—		
		1 Oxygen—		
	1 Sulphurous acid		1 Sulphuric acid	2 Sulphate of soda
	1 Sulphurous acid		1 Sulphuric acid	
	2 Soda			

Monosulphite of Soda, $NaO, SO_2 + 7HO$.

Preparation.—When an aqueous solution of bisulphite of soda is heated until sulphurous acid ceases to be evolved, evaporated, and set aside to crystallize, monosulphite of soda results. The crystals of this salt belong to the rhombohedral system, and effloresce or evolve their water of crystallization if exposed for a few days to the air. When monosulphite of soda is fused, no sulphurous acid is evolved; but its elements recombine amongst themselves, forming sulphide of sodium and sulphate of soda.

Hyposulphite of Soda, $NaOS_2O_2$.—This compound has acquired great importance in the arts of daguerreotype and calotype, and is now made in large quantities.

Preparation.—The best means of generating hyposulphite of soda is the following:—Digest sulphite of soda with sulphur until no more sulphur is dissolved; filter the clear liquor, evaporate, and set aside to crystallize.

Properties.—Hyposulphite of soda, and the soluble hyposulphites generally, possess the remarkable property of dissolving metallic oxides—especially oxide of silver—in considerable quantities, without giving rise to any tangible compound. With silver the result of this action is especially remarkable, the resulting solution being incapable of yielding a precipitate with chlorine, hydrochloric acid, or the soluble chlorides. All the hyposulphites are decomposed on the addition of a stronger acid. Immediately, however, the acid is liberated, it separates into sulphurous acid, which is evolved, and sulphur, which deposits.

Carbonates of Soda, $NaCO_2 10HO$.—There are three known combinations of carbonic acid with soda—the *mono* or neutral carbonate, the bicarbonate, and the sesquicarbonate.

Neutral Carbonate of Soda.—Formerly this salt, large quantities of which are consumed in various operations, was prepared by lixiviating the ashes of sea-weeds (kelp), or the ashes of certain plants growing near the sea (barilla). At present very little carbonate of soda is obtained from either of the above sources, vast quantities being made from sea-salt by the process of Leblanc, already indicated. The operation consists of three different stages of manufacture. The first consists in decomposing sea-salt by means of sulphuric acid, the result of which treatment is the generation of hydrochloric acid and sulphate of soda; the second consists in decomposing the sulphate of soda by heating in reverberatory furnaces a mixture of this substance with carbonate of lime and carbonaceous matter; and the third in lixiviating and evaporating the product. The evaporation in practice is usually carried to the extent of determining the formation of a pellicle on the liquor, which is then poured into a tank, and allowed to crystallize. When the treatment is as thus described, the resulting crystals contain ten equivalents of water of crystallization; but if the crystals be caused to form in a hot liquor still under process of evaporation, the amount

of water which they contain is smaller. Crystals of carbonate of soda dissolve in twice their weight of cold, but in their own weight of boiling water. Exposed to the air, they deliquesce, evolving their water of crystallization, and crumbling to powder. Carbonate of soda, when heated, fast dissolves in its own water of crystallization, undergoing the watery fusion; it then undergoes a second fusion, and becomes anhydrous carbonate of soda.

Bicarbonate of Soda, $NaO\ 2CO_2 + HO$.—This salt may be prepared by transmitting a current of carbonic acid gas through a concentrated solution of monocarbonate; a second equivalent of carbonic acid is absorbed, and bicarbonate of soda, being more insoluble than the preceding salt, falls. Bicarbonate of soda is also prepared by transmitting a current of carbonic acid gas through crystals of the neutral carbonate undissolved.

Sesquicarbonate of Soda, $2NaO,\ 3CO_2 + 4HO$.—A crystalline sesquicarbonate of soda having the above composition is found as a natural product in many parts of the world, especially Egypt, Mexico, and India. The crystalline sesquicarbonate does not effloresce in the air.

Nitrate of Soda.—Nitric acid unites with soda in only one proportion, constituting nitrate of soda or cubic nitre. It may be obtained directly by dissolving carbonate of soda in nitric acid, and crystallizing the residue; but it is seldom produced thus, being generated spontaneously in Peru and some other parts of the world.

Phosphates of Soda.—I have already, under the head of *phosphoric acid*, pointed out the three peculiar modifications which this acid may assume, and which are known respectively by the terms monobasic or metaphosphoric acid, bibasic or pyrophosphoric acid, and tribasic or ordinary phosphoric acid. Each of these modifications of phosphoric acid combines with soda in more than one proportion; consequently there are several phosphates of soda.

First or Ordinary Tribasic Phosphate of Soda, $2NaOPO_5 + 25HO$, or, seeing that one equivalent of water entering into its composition is differently circumstanced to the rest, $(2NaO + HO)\ PO_5 + 24HO$.

Preparation.—When bone ashes are treated with oil of vitriol, the resulting solution contains superphosphate of lime. If carbonate of soda be added to this solution until all deposition of carbonate of lime ceases, and the supernatant solution evaporated until the formation of a pellicle, and then allowed to cool, crystals of tribasic phosphate of soda deposit. It exercises an alkaline reaction on turmeric and reddened litmus-paper. Exposed to the air it effloresces, and dissolves in two parts of boiling and four of cold water. If exposed to heat, it loses its water of crystallization; and if redissolved in water and the solution recrystallized, the original tribasic salt is reproduced, *provided the heat of fusion was not too high*. The effects of this excess of heat in generating a bibasic phosphate have already been indicated.

Second Tribasic Phosphate of Soda, $3NaO,\ PO_5 + 24HO$.

Preparation.—By adding an excess of carbonate of soda to the preceding phosphate, and evaporating the result until crystals form.

Third Tribasic Phosphate of Soda, $3(NaO + 2HO)\ PO_5 + 2HO$.

Preparation.—By adding an excess of phosphoric acid to the first or ordinary tribasic phosphate, and evaporating until crystals form. All the three salts just described give yellow precipitates with nitrate of silver.

Bibasic Phosphate of Soda (Pyrophosphate of Soda), $2NaOPO_5 + 10HO$.

Preparation.—By igniting common phosphate of soda, dissolving the result of

ignition in water, and recrystallising. The existence of another bibasic phosphate has been determined, containing an equivalent of basic water; but it has not been obtained in crystals.

Monobasic Phosphate of Soda (Metaphosphate of Soda), $NaOPO_5$.

Preparation.—By exposure to a high temperature, either the acid tribasic phosphate, or the substance next to be described (microcosmic salt). It is deliquescent and fusible, readily soluble in water, but does not form crystals.

Phosphate of Soda and Ammonia (Microcosmic Salt), $NaO, NH_4O, HO, PO_5 + 8HO$.

Preparation.—By dissolving six parts of common phosphate of soda in two of water, then adding one part of sal-ammoniac in powder, separating by a filter the common salt which deposits, and evaporating the filtrate. Microcosmic salt is a flux of great value, especially in conducting blowpipe operations, for which purpose it is often employed.

Biborate of Soda (Borax), $NaO, 2BO_3 + 10HO$.—Under the head of *boracic acid* (page 379) the commercial source of native biborate of soda has been indicated. Considerable quantities, however, are manufactured by saturating the native boracic acid of Tuscany with carbonate of soda. Borax crystallizes in six-sided prisms; the crystals are soluble in twenty parts of cold and six parts of boiling water. Borax is a valuable flux; when mixed with oxide and metallic substances generally it lowers their point of fusion, and gives rise to transparent vitreous compounds. The ease with which borax dissolves metallic oxides when fused in contact with them, renders it valuable in the operations of soldering and brazing. In performing these operations it is absolutely necessary that the surfaces to be joined be perfectly free from all adherent oxide; this is accomplished by the use of borax, which, melting in contact with the oxides, fuses them away. Borax may be regardad as filling in the operations of igneous chemistry, a parallel function to water in operations by the moist process. The constitution of borax is acid, as may be seen by simply inspecting its formula; nevertheless, it acts like an alkali on test paper, and thus furnishes an example of the futility of pronouncing on the questions of neutrality or the reverse from appearances characteristic of free acidity and free alkalinity.

Sulphurets (Sulphides) of Sodium.—Of these there are several; the monosulphuret or monosulphide, NaS, is prepared similarly to the monosulphuret or monosulphide of potassium. It may be obtained in crystals, but soon decomposes by contact with the air into hydrate and hyposulphite of soda.

Chloride of Sodium (Common Salt), Na Cl.—This most important salt may be formed directly for the purpose of demonstration, by saturating either carbonate of soda, or hydrate of soda, with hydrochloric acid, and evaporating the fluid until crystals form. When chloride of sodium absolutely pure is required for certain purposes of chemical experiment, the above is the best method of procuring it. Nature, however, supplies it to us ready made, and in quantities which are inexhaustible. In many parts of the world it is obtained by evaporating sea-water; in others it is procured from beds of rock-salt. Generally speaking, rock-salt does not furnish chloride of sodium sufficiently pure for culinary use. The plan of obtaining white salt from coloured rock-salt, is as follows:—Pits or wells are dug into the salt-bed, and into these pits water is allowed to accumulate and remain until it becomes fully saturated. During its act of solution various metallic oxides, especially oxide of iron, which is associated with chloride of sodium in rock-salt, deposits, yielding a comparatively pure and colourless solution above; this, on being subjected to evaporation, yields white table salt.

Alkalimetry.—This term is applied to the operation of determining the percentage amount of soda or potash in a given quantity of impure carbonate or hydrate of soda, or potash, such as we find in soda ash, barilla, kelp, or potash, as the case may be. These products vary as to composition between very wide extremes; but their effective constituents are hydrate, and carbonate of alkali—potash or soda.

From a consideration of the laws of definite chemical combination, it follows that the relation between a given base and the necessary amount of acid to neutralize that base and form a given result, is fixed and invariable. For example, inasmuch as the combining equivalent of sulphuric acid is forty, and of soda thirty-one,* it follows that an unknown weight, which we will call x of soda capable of neutralizing 40 grains of sulphuric acid must be equal to 32 grains. Again, inasmuch as the combining equivalent of potash is 47, it follows that an unknown quantity (x) of potash must be equal to 47 grains. On the consideration of these facts is based the ordinary method of alkalimetry; which consists in the addition of dilute sulphuric acid of known strength to a given weight of alkaliniferous compound, and noticing the amount of acid employed for its neutralization, as indicated by test paper. The amount of acid used may be determined by weighing or by measuring, the latter process being most generally adopted.

Preparation of Alkalimetric Sulphuric Acid.—It is obviously indispensable to begin by forming test acid of determinate strength—the proportions of one part (weight) in ten parts of fluid—in other words, one part to nine parts of water are generally adopted. If the oil of vitriol happen to have a specific gravity of 1·85, it will be a monohydrate, and the process of converting it into test acid is simple enough. Inasmuch as 49 grains of monohydrate of sulphuric acid contain 40 of real acid, the quantity of the latter required in the imperial gallon of 70·000 will be, of course, $\frac{70{\cdot}000}{10}$, or 7000 grains. Now 7000 grains of real acid correspond with 8574· grains of the monohydrate, as the following proportion demonstrates:—

$$40 : 49 :: 7000 : 8574.$$

Hence, 8574 grains of monohydrate of sulphuric acid being weighed out, and diluted with the necessary amount of water to make up the gallon, the result is the test acid required.

If, however, the oil of vitriol employed be weaker than the monohydrate, a condition indicated by its having a less specific gravity than 1·85, the process of bringing it to the condition of test acid is more troublesome. The first step consists in ascertaining its exact strength by a process the exact reverse of alkalimetry—namely, by seeing how much alkali of definite and known composition it is capable of neutralizing. Pure anhydrous carbonate of soda is used for this purpose. Its atomic or equivalent number is 53, hence every 53 parts of this salt neutralized will be indicative of 40 parts of real sulphuric acid expended in effecting the neutralization. These data furnish the means of learning the strength of the sulphuric acid employed by a very obvious proportion.

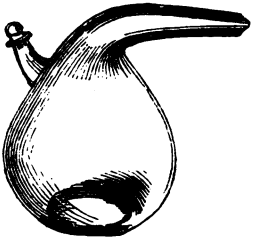
The Alkalimeter. Variety 1, *Measuring Alkalimeter.*—This consists of a glass tube about fifteen inches long and about half an inch internal diameter, capable of holding 1000 grains of water at 60° Fah., and graduated in divisions of one grain. In its simplest form, the alkalimeter is simply a tube such as described, furnished with a lip or spout; but a still better construction is represented in the following cut.

* Omitting fractions; *vide* table at p. 279.

Let us now assume that the determination is required of the amount of effective soda in a specimen of soda-ash. A given quantity, say 50 grains, is to be accurately weighed, dissolved in warm water, and if it contain much mechanical impurity, filtered. The alkalimeter is next filled to the extent of its scale with test acid, and portions of this are carefully added to the soda solution until complete neutralization has been effected. This point may be known to have been attained when, after warming the tested solution to expel carbonic acid, and allowing it to remain at rest a few minutes, it no longer affects litmus-paper, either blue or reddened. If we assume that 29 measures or grains of test acid have been appropriated, then we learn that the soda-ash examined holds 44·8 per cent. of effective alkali, by the following proportional statement:—

$$40 : 31 :: 29 : 22{\cdot}4.$$

Variety 2, *Weighing Alkalimeter.*—This instrument consists of a thin bulb of glass drawn into a fine, almost capillary, beak, and supplied with a ground and stoppered tubulure. It is, in point of fact, a miniature retort, as the accompanying woodcut represents. A glance at the construction of this instrument will show that it is well adapted for the purpose intended. The instrument having been charged with test acid, and the weight of the instrument and acid determined, the stopper is removed, and portions of the acid are dropped out until the alkaline fluid has been completely saturated. The instrument is now weighed again, the amount of acid expended noticed, and the corresponding amount of alkali determined by an obvious sum of proportion.



Occasionally it is desirable not only to know the joint amount of hydrate and carbonate of an alkali present in any given sample, but the amount of each. In this case, the following plan may be adopted.

By means of a bent glass tube and perforated cork, the larger tube C, holding pieces of fused chloride of calcium, is attached to a small flask. Into this flask has been previously poured the alkaline solution, and a small test tube has been lowered in such manner that, at the operator's pleasure, its contents (dilute sulphuric acid) may be mingled with the alkaline solution. Before this is done, the whole apparatus is accurately weighed, and the weight noted. It is now removed from the balance-pan, and the acid is mingled with the alkaline liquor. Decomposition of course ensues, and carbonic acid is evolved. Passing through the

tube holding chloride of calcium, it loses itself in the air; meanwhile any small amount of aqueous vapour which might accompany the gas can get no further than the chloride of calcium, that material having such a powerful tendency to unite with water. But the most important function of the chloride of calcium is this:—The apparatus at the present stage of our operation necessarily contains some of the carbonic acid evolved; we desire to expel that carbonic acid, and accomplish the result as follows:—The flask is heated until it becomes charged with vapour; this necessarily pushes the carbonic acid before it, and would itself follow were it not for the protecting chloride of calcium, which restrains it. The apparatus is now permitted to cool, and is weighed once more; the deficiency of weight is the weight of carbonic acid expelled. Twenty-two parts of carbonic acid correspond with forty-five of carbonate of soda.

The preceding operation is unexceptionable if an alkaline sulphite, hyposulphite, or sulphuret be absent; but the presence of either of these gives rise to inaccuracy. A preliminary experiment serves to convey the necessary information in this particular. Sulphurous acid, like carbonic, is expelled from sulphites and hyposulphites by the addition of a stronger acid; but it may be easily distinguished from carbonic acid by its smell, which resembles that of burning sulphur. Sulphurets, too, are easily recognised by the nauseous smell of sulphuretted hydrogen, liberated on the addition of an acid.

If on testing a portion of alkaline fluid which is intended to be subjected to the process of alkalimetry under consideration, either sulphurous acid or sulphuretted hydrogen be developed, the following means must be had recourse to for obviating inaccuracies springing from these sources:—A teaspoonful of yellow chromate of potash must be added to the alkaline solution before pouring it into the test-bottle; by which treatment both sulphuretted hydrogen and sulphurous acid will be decomposed at the moment of their liberation, sulphur being deposited in either case, and all possibility of error from the above-mentioned causes obviated. Theoretically, the presence of chlorides in the alkaline solution under examination should be productive of embarrassment; practically, however, they are not, the solution being so weak that all the hydrochloric acid resulting from the chlorides when decomposed is absorbed, and retained. For other particulars relative to this process of alkalimetry, I must refer to the original work of Fresenius on the subject. It has been translated into English by Mr. Lloyd Bullock.

GENERAL REMARKS ON POTASH AND SODA, AND THE SALTS OF TRUE ALKALINE METALS.

The reader will have remarked that a very striking resemblance subsists between the true alkaline metals already described and also between their respective combinations. The more striking this resemblance, the greater is the necessity for mastering the few special distinctions which do exist, and which not only enable us to distinguish as between combinations of potassium and sodium respectively, but to separate them from each other. The following are the chief distinctive characteristics known to the chemist:—

Salts of potassium, and potash, sodium, and soda do not yield a precipitate with carbonic acid or alkaline carbonates—do not evolve ammonia when a strong acid is added—do not, if colourless themselves, yield a coloured precipitate with hydrosulphuric acid or hydrosulphate of ammonia.

Combinations of Potassium and Potash.

Tinge flame, blue.

Yield a precipitate, in virtue of their metallic constituent, with—

Tartaric acid.
Perchloric acid.
Hydro-fluosilicic acid.
Chloride of platinum.

Combinations of Sodium and Soda.

Tinge flame, yellow.

Are sometimes described as yielding no precipitate, in virtue of their metallic constituent, with any reagent whatever; but *do* yield a precipitate with antimonic acid.

LITHIUM.

Atomic weight . . . 6·43

Preparation.—Lithium was developed from its oxide lithia by voltaic agency. It may, probably, be capable of production, as potassium and sodium are produced on the large scale.

Quite recently Liebig has published a method of obtaining lithium in considerable quantities from the fused chloride of lithium. The salt is placed in a crucible of porcelain attached to the negative terminal of a voltaic battery, and fused; the negative terminal or pole, which is of iron wire, and about the size of a knitting-needle, is now brought in contact with its surface, when decomposition immediately ensues, and metallic lithium attaches itself to the end of the wire. As one portion of metal is thus obtained, it may be detached by an iron spoon, and thrown into Persian naphtha, on the surface of which it floats, lithium, in point of fact, being the lightest known solid in nature.

Properties.—A white metal resembling sodium in its physical and chemical characteristics.

Compounds.—Oxide of lithium, or lithia, LO. This body stands in the same relation to lithia as soda to sodium, and potash to potassium. It is a rare compound, being specially denominated in the mineral kingdom, and is chiefly interesting as furnishing the connecting link between the true fixed alkalies (potash and soda) and the earths. The principal minerals in which lithia is found are some varieties of tourmaline, ampligonite, lepidolite, and spodumene. There are various processes for extracting lithia from these minerals, and all involve a difficulty, springing from the same cause namely, the necessity of avoiding soda and potash in every part of the analytical process. As a general rule, the first part of every analysis of a siliceous mineral, insoluble in acids (*some* siliceous minerals are soluble), consists in levigating it with potash or soda, or the carbonates of one or both of these alkalies, and fusing the mixture in a platinum crucible. From this plan of treatment, where the object is to extract lithia, we are debarred; because if lithia were once mixed with any compound of the preceding alkaline metals, the difficulties attendant upon their separation would be enormous. Though the processes which have been suggested for the isolation of lithia are numerous, they admit of being reduced to two generalizations. The first consists in substituting an alkaline earth, or a carbonate of an alkaline earth, for a real alkali or its carbonate, in the preliminary operation of fusion; the second, which is by far the more elegant, consists in removing all the silica in the form of gaseous fluoride of silicon.

Scheme 1.—Petalite is to be reduced to an impalpable powder, then mixed with five or six times its own weight of carbonate of lime, or of baryta, and heated to whiteness

in a platinum crucible placed in an earthen one, with a layer of magnesia between the two, for the space of one hour. The resulting mass is next digested in hydrochloric acid moderately diluted, evaporated to dryness; taken up once more by dilute hydrochloric acid, and filtered for the purpose of removing silica (page 382). The solution is next mixed with excess of carbonate of ammonia, boiled, and filtered; the filtrate evaporated to dryness, and heated in a platinum crucible, by which means hydrochlorate of ammonia is expelled, and fused sulphate of lithia remains. From the sulphate the salts of lithia may be prepared.

Scheme 2.—Petalite being finally levigated as before, is mixed with twice its weight of fluor-spar, and the whole formed into a paste with strong oil of vitriol. The operation requires a platinum dish. Heat is now applied, and all the silicic acid is evolved in the condition of fluo-silicic acid gas. The solid fixed result is a mixture of sulphate of lime with sulphate of lithia. The latter may be dissolved out by a mixture of alcohol and water, a menstruum in which sulphate of lime (gypsum) is insoluble.

Hydrate of lithia, although having most general similarity to the hydrates of potash and of soda, is more insoluble than either, thus manifesting an approach to the class next to be treated of—namely, the alkaline earths—like which, also, it forms sparingly soluble combinations with carbonic and phosphoric acids.

TERRIGENOUS METALS—BARIUM.

Equivalent or atomic weight . . . 68·5

History.—Barium was discovered by Sir Humphry Davy, who obtained it by subjecting baryta to voltaic decomposition. It may be obtained more readily by transmitting vapour of potassium through baryta (oxide of barium), contained in an iron tube strongly heated. Baryta by this treatment is decomposed, potash being formed and barium liberated. The mixture of potash and barium is now triturated with mercury, by which means a barium amalgam is formed; this being subjected to heat in a small retort of green glass, containing hydrogen or nitrogen, mercury distils over, and barium remains.

Properties.—These are very similar to those of the alkaline metals already described. Barium is yellowish white, something the colour of silver, malleable, fusible at a heat below redness, decomposes water, though not so violently as potassium and sodium; and, if exposed to the air, soon becomes coated with a white crust of protoxide of barium, or baryta.

Protoxide of Barium (*Baryta*), BO—Originally this compound was termed barytes, but it is now called *baryta* for the sake of uniformity. The designation *baryta* comes from Βαρυς, heavy, on account of the great weight of native sulphate, and carbonate of baryta.

Preparation.—Pure baryta cannot readily be obtained from the carbonate by subjecting the latter to heat, as is the case with lime, in consequence of the tenacity with which the carbonic acid is retained. The best method of preparing it consists in decomposing the nitrate at a red heat in a large porcelain crucible, by which treatment the constituents of nitric acid are evolved, and baryta remains.

Properties.—A dirty white or gray substance, fusible at high temperatures, and manifesting a great tendency to combine with water, and form the compound next to be described.

Hydrate of Baryta.—This compound may be prepared either by treating anhydrous baryta with water, or by boiling a solution of sulphide of barium with copper, in which case the metal removes the sulphur, forming an insoluble sulphide of copper, and solution of hydrate of baryta remains. By evaporation it may be obtained in the crystalline state. It contains 10 equivalents of water, and hence its formula is $BaO + 10HO$. When the crystals are heated they evolve 9 equivalents of water, leaving the monohydrate, a substance which cannot be decomposed by heat. The solution of hydrate of baryta is strongly alkaline; by exposure to the atmosphere it rapidly attracts carbonic acid, and generates carbonate of baryta.

Peroxide or Binoxide of Barium.—Preparation: When baryta (protoxide of barium) is heated in oxygen gas, at temperatures between 550° and 750° Fah., a second equivalent of oxygen is absorbed, and binoxide of barium results.

Properties.—In physical appearance this substance resembles baryta, only its colour is slightly darker. It readily combines with water, forming a hydrate of uncertain composition; by boiling this solution oxygen gas is evolved, and hydrate of baryta remains.

Salts of Baryta.—*Sulphate of Baryta.*—This compound is found in nature, and is also readily formed by artificial processes. Whenever sulphuric acid, or a sulphate is brought into contact with a solution containing baryta, or barium, in any form of combination, sulphate of baryta results, and is deposited. Native sulphate of baryta is called *heavy spar*, its specific gravity is 4·4. Sulphate of baryta is remarkable for its extreme insolubility. In water, hot or cold, it is *quite* insoluble; and even hot nitric and hydrochloric acids dissolve but the faintest traces. Owing to the tendency of baryta to combine with sulphuric acid, solution of hydrate of baryta, and barytic salts generally are valuable agents for the separation, and quantitative estimation, of sulphuric acid. Conversely, sulphuric acid and soluble sulphates are employed for the separation and estimation of baryta. Sulphate of baryta is a compound of one equivalent of acid and base; hence, every 116·64 parts of the salt correspond with 40 of real sulphuric acid and 76·5 of baryta.

Nitrate of Baryta.—This salt is of extensive application in the laboratory as a chemical re-agent; it may be prepared directly by saturating either baryta, or hydrate of baryta with nitric acid, and crystallizing the solution by evaporation. A similar final result occurs when carbonate of baryta is substituted for the preceding; occasionally, however, in practice, nitrate of baryta is prepared from the native sulphate indirectly as follows. Native sulphate of baryta, finely powdered, is mixed with about one-tenth its weight of finely divided charcoal; a sufficient quantity of oil is now incorporated with the mixture to form a stiff paste, which is heated in a crucible to redness. Decomposition ensues, and sulphuret (or sulphide) of barium, intimately mixed with charcoal, remains. The mixture is now lixiviated with water, which dissolves out the sulphide of barium and leaves the charcoal. Nitric acid is now added to the solution of sulphide of barium, by which treatment further decomposition is effected; hydrosulphuric acid being evolved, and nitrate of baryta formed. The latter salt may be obtained in crystals by evaporation.

Carbonate of Baryta.—This salt is found native, being known by the name of *Witherite;* it may also be readily formed by the double decomposition of a soluble baryta salt, by means of a soluble carbonate, or by the transmission of carbonic acid gas through a solution of hydrate of baryta. At a very high temperature carbonate of baryta fuses and evolves its carbonic acid; but at a temperature short of fusion this

decomposition does not ensue: hence, carbonate of baryta cannot be made to yield baryta by the mere process of kiln-burning, as is the case with lime.

Sulphides or Sulphurets of Barium.—There are several of these compounds, but the exact number has not been determined. Monosulphide of barium is a crystalline compound, it may be obtained by carefully evaporating the lixiviated result of heating sulphate of baryta with charcoal. The higher sulphur compounds of barium are more or less yellow, and may be prepared by digesting a solution of the monosulphide with sulphur.

Chloride of Barium.—This very important salt may be prepared by the direct saturation of baryta, or carbonate of baryta with hydrochloric acid; on evaporating the solution, chloride of barium is deposited, in the crystalline form. It contains one atom respectively of chlorine and of barium, combined with two atoms of water; hence it is represented by the formula $BaCl + 2HO$. By the application of heat, the water is driven off and anhydrous chloride of barium remains. In practice, on the large scale, chloride of barium is prepared indirectly, by calcining in a reverberatory furnace a mixture of two parts of powdered sulphate of baryta, and one of chloride of calcium. The results of this decomposition are sulphate of lime and chloride of barium. The latter being very soluble in water, whilst the former is not, separation of the two may be readily effected.

General Characteristics of Baryta and its Combinations.—The two most leading characteristics of this class of bodies have already been indicated—namely, their tendency to form carbonate and sulphate of baryta. In addition to these peculiarities the following should be remembered by the chemist. The salts of baryta yield no precipitate with ammonia, provided the latter be completely free from carbonic acid. The most likely substances to be mistaken for barytic salts in solution are solutions of lead and strontium, both of which afford white precipitates with carbonic acid and carbonates, sulphuric acid and sulphates, resembling by general appearance those produced by barytic compounds. Lead, however, the student will remember, is a *calcigenous* metal; its compounds blacken solutions of hydrosulphuric acid or hydrosulphates, which baryta and solutions of barytic salts do not; thus between these two classes there is a ready means of distinction. As between solutions of barium and strontium, the means of distinction will be rendered apparent when strontium shal come under our notice; meanwhile the fact may be indicated that barytic compounds have the property of imparting a greenish tint to flame.

STRONTIUM.

Equivalent or atomic weight . . . = 43·8

General Remarks.—This metal very closely resembles barium in its genera qualities—a resemblance which holds good as between the various parallel combinations of the two metals. The term *strontia* is derived from the name of the locality *Strontian*, in Scotland, where the carbonate of the oxide of strontium (strontia) is found native. There is also a native sulphate of strontia (oxide of strontium); its mineralogical designation is *celestine*.

Preparation.—Exactly like barium from baryta.

Properties.—Almost the same as those of barium.

Compounds of Strontium with Oxygen, Protoxide of Strontium, or Strontia.—This earthy oxide is prepared by processes so exactly resembling those already enumerated

under the head of baryta that it is unnecessary to particularize them. Like baryta, it forms a crystalline hydrate with water, having the composition of $Sr_2O + 10HO$.

Binoxide of Strontia may be procured by the addition of peroxide (binoxide of hydrogen) to a solution of hydrate of strontia; under which circumstances it deposits in the form of small crystals.

Salts of Strontia.—Protoxide of strontium, or strontia, performs the part of a very powerful base, combining with most acids, and giving rise to well-defined salts.

Nitrate of Strontia.—This salt is prepared by parallel operations to those already described under the head of nitrate of baryta. It readily crystallizes; if evaporated by application of heat, the crystals are anhydrous; but if evaporated in vacuo, the crystals retain five equivalents of water. Nitrate of strontia is much employed in pyrotechnic art, for the purpose of communicating a red tint to certain fireworks.

Carbonate and Sulphate of Strontia.—These salts are exceedingly similar to those of baryta, and need no further description. A similar remark also applies to the *sulphides of strontia. Chloride of strontium* may be prepared by processes corresponding with those employed for the preparation of chloride of barium, from which it may be distinguished by the property of readily dissolving in alcohol, whereas chloride of barium is insoluble in that menstruum. Crystallized chloride of strontium holds six equivalents of water, and its formula consequently is $SrCl + 6HO$.

General Characteristics of Strontia and its Combinations.—The soluble compounds of strontium and strontia, yield no precipitate with pure ammonia, but are precipitated by carbonate of ammonia, and alkaline carbonates generally. They yield a very insoluble white sulphate with sulphuric acid, and soluble sulphates generally, which can hardly be distinguished from sulphate of baryta, except by the aid of collateral tests. It is, however, rather more soluble in water than sulphate of baryta. Hence, if sulphate of strontia be boiled with water, filtered, and tested with a soluble salt of baryta, sulphate of the latter base is generated. The other distinctive characteristics as between barium and strontium, and their respective combinations may be thus stated:—

Barium and its Combinations.	*Strontium and its Combinations.*
Tinge flame green.	Tinge flame red.
Chloride, insoluble in alcohol.	Chloride, soluble in alcohol.
Chromate of potash gives a yellow precipitate.	Chromate of potash gives no precipitate.
Hydrofluosilicic acid yields a precipitate.	Hydrofluosilicic acid yields no precipitate.

CALCIUM.

Equivalent or atomic weight . . 20

General Remarks.—This metal is very widely diffused through nature in the form of oxide of calcium (lime) variously combined; especially with carbonic and sulphuric acids, constituting respectively carbonate and sulphate of lime. Calcium is obtained by processes similar to those for obtaining barium and strontium, and in physical appearance it much resembles these metals.

Compounds of Calcium with Oxygen.—There are two known oxides of calcium. One the well known *protoxide*, or *lime*, the other having the composition of $Ca\,O_2$, and, therefore, appropriately termed the binoxide or peroxide.

Protoxide of Calcium (*lime*).—This oxide is readily prepared by strongly heating any

of the native carbonates of lime, such as Iceland spar, marble, chalk, or any of the various rocks to which the generic term limestone is applied.

When desired quite pure, the best material from which to obtain lime is Iceland spar; but white statuary marble is nearly as pure, and far less expensive. Absolutely pure lime may also be obtained by calcining nitrate of lime, as was directed in the case of baryta and strontia. Lime is whiter than either baryta or strontia, and, like them, highly caustic; like them, too, it may be precipitated from its solutions by means of sulphuric acid and sulphates, though not so readily; and not except certain precautions be taken, which will be mentioned further on. From a consideration of these facts, we learn that carbonate and sulphate of lime are far less insoluble than the corresponding salts of baryta and strontia. Lime cannot be fused by the strongest furnace heat, and it is almost infusible in the oxy-hydrogen flame. Lime, like baryta and strontia, combines with water, and forms many hydrates. During this process of combination, much heat is evolved. When only sufficient water has been added to make the lime crumble to powder, the result is called slaked lime; when enough is added to form a paste, this is called cream of lime; and a colourless solution of lime in water is called lime-water. The quantity of lime capable of being dissolved by water is very minute, not exceeding one part in a thousand, and still less if the water be hot: for lime presents the remarkable condition of being more soluble in cold than in hot water. Lime-water, when prepared, must be preserved from atmospheric contact, otherwise it absorbs carbonic acid, and forms *carbonate of lime*. The applications of lime are numerous and important. It constitutes the basis of all aërial, and the greater number of subaqueous mortars, and is extensively employed as a fertilizer. The theory of the hardening of mortars partly depends on the lime absorbing carbonic acid, and becoming carbonate, and partly on its dissolving silica, and generating silicate of lime. When the latter compound exists below a certain limit, the mortar is readily disintegrated by water, but when the quantity of silicate of lime preponderates, and more especially where it is mixed with certain amounts of silicate of iron and alumina, it is no longer attacked by water, and thus forms a subaqueous cement.

Sulphate of Lime.—This compound may be directly formed by the addition of sulphuric acid to lime or carbonate of lime, or by mixing any soluble lime or calcium salt with sulphuric acid or any soluble sulphate.

The remark has already been made, that sulphate of lime is far less insoluble than the sulphates of baryta and of strontia; one part, in point of fact, dissolves in about 300 of water, hence lime does not admit of being completely thrown down from a mere aqueous solution of lime salt by mere addition of sulphuric acid or a soluble sulphate. If alcohol, however, be added to the solution in certain proportions, the sulphate of lime may be completely deposited, a circumstance which is frequently taken advantage of in analytical chemistry.

It is the native sulphates of lime, however, which claim most especially our attention. Native sulphate of lime occurs in two forms—anhydrous and hydrated. The former is known by the mineralogical term *anhydrite*, and the latter is called *Plaster of Paris*, or *Gypsum*. This compound, when quite pure, is a binhydrate, and is, therefore, represented by the formula $Ca_1, SO_3 + 2HO$. It is rarely found quite pure, however, generally containing variable portions of clay and carbonate of lime. When gypsum is carefully heated at temperatures from 250° Fah. to 270° Fah., its water is evolved, and anhydrous sulphate of lime remains. This latter substance is much employed for the purpose of taking casts, and the theory of its action is simple. It

chemically unites with water, and again returns to the condition of hydrated sulphate of lime. Occasionally gelatinous matters are dissolved in the water employed, and for some purposes alum is calcined with gypsum. Alum plaster does not set very quickly, but, when once set, the result is more hard and durable than ordinary hardened plaster; it is therefore preferable for certain purposes, and being somewhat transparent, it is more elegant.

Carbonate of Lime.—Whenever lime-water is exposed to the action of carbonic acid, either alone or mixed, or whenever a soluble salt of lime or calcium is mixed with a soluble carbonate, carbonate of lime results. Native carbonate of lime, however, is of the greatest importance, and is very widely diffused through nature. Not only does it constitute large portions of the crust of the earth, but it is diffused in minute quantities throughout the members of the animal and vegetable kingdoms. Native carbonate of lime may be crystallized or amorphous. The former is found in two crystalline systems, constituting two minerals, known respectively as Iceland or calcareous spar, and arragonite. The former belongs to the rhombohedral system of Weiss and Mohs, the second belongs to the right rectangular prismatic system.

The amorphous varieties of carbonate of lime are far too numerous for individualization. The purest variety is white statuary marble.

Carbonate of lime does not dissolve in pure water in any appreciable quantity; but it readily dissolves in water containing carbonic acid. This fact renders easy of comprehension a frequently-observed phenomenon, occurring when certain waters, rich in carbonic acid, and filtrating through calcareous beds, are boiled. Under these circumstances, a crust of carbonate of lime is deposited, owing to the evolution by heat of the carbonic acid in which it was dissolved. On the small scale, boiling becomes an efficient means by which carbonate of lime may be caused to deposit from the waters in question; but to large bulks of water it is obvious this treatment will not apply.

To Dr. Clarke, we are indebted for another plan of accomplishing the same result. Instead of dissipating the excess of carbonic acid by heat, he removes it by the addition of a further amount of lime, by which treatment the original amount of super-carbonate of lime (whatever be its exact atomic constitution) is reduced to the state of monocarbonate; being thus necessarily rendered insoluble in water it deposits.

Phosphates of Lime.—There are numerous compounds of phosphoric acid, in its three modifications with lime. The chief phosphates of lime which have been studied are the following.

Biphosphate of Lime, improperly so called.—This salt has a formula of $(CaO + 2HO)PO_5$, and is generated by treating bone earth with sulphuric acid, separating the sulphate of lime which deposits, and evaporating the filtered liquor. The phosphate in question then crystallizes.

Phosphate of Lime, having the formula of $(2CaO + HO)PO_5 + 4HO$. This salt is generated by adding ordinary commercial phosphate of soda $(2NaO + HO)PO_5 + 24HO$ to any soluble salt of lime. It is a white gelatinous substance.

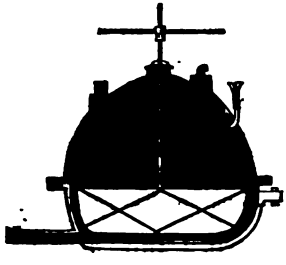
Phosphate of Lime, having the formula of $3CaOPO_5$.—This salt may be prepared by digesting the preceding compound with ammonia, which dissolves a portion of phosphoric acid; or by adding an excess of phosphoric acid to a solution of chloride of calcium, and supersaturating the mixture with ammonia. This is the phosphate of lime which exists in bones, and also in a native mineral species termed apatite. Bone

ashes are composed of this phosphate, mixed with carbonate of lime in the proportions of ⅔ths and ⅓th.

Metaphosphate of Lime.—This salt is represented by the formula $CaO_1\ PO_5$, and is generated by heating the biphosphate $(CaO + 2HO)PO_5$ to redness.

Chloride of Lime, improperly so called. When slaked lime is exposed to the action of chlorine, the latter is absorbed, and a pulverulent material, known in the arts as *chloride of lime*, results. The material is extensively employed in bleaching operations, in some varieties of calico printing by the process of *discharge*, as it is appropriately termed, and for numerous other purposes. The so-called chloride of lime of commerce is not a definite compound; but the material on which the effective property depends is hypochlorite of lime. If commercial chloride of lime be treated with water, hypochlorite of lime is dissolved out. It may be also directly formed by the admixture of hypochlorous acid with cream—or milk—of lime; the latter must, however, be in excess, otherwise the hypochlorite of lime is decomposed into chlorate of lime, and chloride of calcium.

Chlorometry.—This term may be correctly applied to the estimation of chlorine generally—more usually, however, it is restricted to the specific case of estimating the effective amount of chlorine in commercial bleaching-powder, or the so-called chloride of lime. The first method employed was based on the estimation of the amount of indigo susceptible of decolouration by treatment with a definite amount of bleaching-powder; but that process having been found incorrect, it has given place to a process founded on the property which chlorine has of converting arsenious into arsenic acid. The following proportions of materials are recommended by Sir Robert Kane, and are found to answer well in practice. Dissolve 100 grains of arsenious acid in 2000 grains of strong hydrochloric acid, and the liquor diluted with distilled water until it occupies the volume of 700 grains of water. The liquid thus constituted is the standard test liquor, which is used as follows:—Diffuse 100 grains of the commercial substance to be examined through 1000 grains of water, and pour upon it the test liquor from a graduated glass tube into a deep jar, continually agitating the mixture. Continue the operation of pouring and agitation, until the decolouring power of the mixture is completely destroyed, a result which is known by testing it, from time to time, with a drop of solution of sulphate of indigo. The absolute quantity of effective chlorine present in 100 grains of commercial chloride of lime examined, is known by dividing the quantity (measure) of the test liquor employed by 100.



Another process, equally good, is as follows:—300 grains of crystalline and dry sulphate of iron are to be dissolved in the requisite quantity of water for bringing the solution to the volume of 5000 grains of water; this is the standard, or test solution. 100 grains of the commercial sample are now weighed out, diffused through water, and the solution of sulphate of iron added in the slightest possible excess, an event known by the solution taking a blue colour when tested with prussiate of potash. By dividing the quantity (measure) of sulphate of iron employed, by 100, the quantity of available chlorine present is arrived at. On the large scale, bleaching-powder is prepared by generating

chlorine in a leaden still, to which an apparatus for stirring, without admitting atmospheric air, is attached.

The best samples of commercial bleaching-powder contain about 30 per cent. of chlorine.

Calcium with Sulphur.—Sulphates or sulphurets of calcium. Of these bodies there are several, but none are of any great importance.

Calcium with Chlorine.—Chloride of calcium. There is only one known compound of chlorine with calcium, and it is of great importance, both as a laboratory agent, and in several arts and manufactures.

Preparation.—When hydrochloric acid is saturated with lime, hydrate of lime, or carbonate of lime, and the mixture evaporated to the necessary extent, crystals are deposited having the following formula—$Ca\,Cl + 6HO$. They may be regarded as hydrochlorate of lime, or chloride of calcium, according to the theory of their constitution adopted. By fusing these crystals in an iron, or still better a platinum vessel, all the water is expelled, and a fused residue remains, which can be no other than chloride of calcium. If the crystallized salt be heated merely to 400° Fah., a porous mass remains containing only two atoms of water. In this state, as well as rendered completely anhydrous by fusion, chloride of calcium is of extensive application in the laboratory as an agent for accomplishing the absorption of water. Crystallized chloride of calcium develops a low degree of temperature during the act of solution in water, and for this reason frequently enters into the composition of freezing mixtures. Chloride of calcium readily dissolves in alcohol, and when the alcoholic solution is evaporated, crystals deposit, holding a portion, at present unknown, of alcohol in their composition.

Calcium with Fluorine (Fluoride of Calcium).—This is the well known Fluor, or Derbyshire spar, so called on account of the property which it has of increasing the fusibility of many other mineral substances when heated in admixture with them.

General characteristic distinctions of Calcium compounds.—The solutions are not precipitated by ammonia, but are readily precipitated by alkaline carbonate. They impart a tawny orange tinge to flame.

When diluted considerably they no longer afford a precipitate with sulphuric acid, and soluble sulphates.

They yield a white precipitate with oxalic acid, and oxalate of ammonia, nearly insoluble in water, and in an excess of oxalic acid. Oxalic acid and oxalate of ammonia may be regarded as the chief separative agents for lime out of the various calcium solutions.

MAGNESIUM.

Preparation.—By decomposing anhydrous chloride of magnesium with potassium or sodium. The decomposition may be effected in a platinum crucible having its lid tied firmly down. A red heat is required.

Properties.—A white metal, something like silver in appearance, not perceptibly oxidised by cold, but rapidly by boiling water.

Magnesium and Oxygen. Oxide of Magnesium (Magnesia).—This is the only compound of oxygen and magnesium known. It results whenever magnesium becomes oxidised, but is prepared in practice by calcining native carbonate of magnesia, also by exposing nitrate of magnesia to an elevated temperature.

Properties.—A white powder infusible in the highest furnace heat, more insoluble than lime in water, and manifesting a distinct alkaline reaction on test-papers.

Magnesia with Sulphuric Acid (Sulphate of Magnesia).—This is the well known Epsom salt, so called from being a constituent of water drawn from a spring in that locality.

Preparation.—Directly by saturating dilute sulphuric acid with magnesia, its carbonate, or the hydrate of its carbonate; also by treating magnesian lime-stone with sulphuric acid, the difference between the solubilities of sulphate of lime and sulphate of magnesia constituting an easy means of effecting the separation of one from the other; indirectly from the sea-water, from which common salt has been deposited.

Sulphate of magnesia forms prismatic crystals, the composition of which is represented by the formula $Mg\ O_1\ SO_3 + 12\ HO$. It combines with alkaline sulphates forming double salts.

Nitrate of Magnesia.—May be found by the direct process. It is an exceedingly deliquescent salt, completely decomposed at a red heat, pure magnesia in a dense form remaining.

Carbonate of Magnesia.—Large quantities of this material are found in nature, both pure, and as a constituent of Dolomite (magnesian lime-stone). For the most part pure native carbonate of magnesia is amorphous, but crystalline specimens exist. A so-called carbonate of magnesia is produced artificially by decomposing solutions of sulphate of magnesia by the addition of an alkaline carbonate. The white gelatinous substance deposited is, however, not pure carbonate of magnesia, but that substance mixed with variable portions of hydrate of magnesia. Carbonate of magnesia, like carbonate of lime, is soluble in excess of carbonic acid.

Phosphates of Magnesia.—There are numerous phosphates of magnesia, most of which have been imperfectly studied. They are all inferior in interest to the double phosphates of ammonia and magnesia, two of which have been individualized.

The first has a composition of

$$[2(NH_3, HO) + HO]PO_5 + (2MgO + HO)PO_5 + 6HO,$$

and may be formed by the addition of a solution of ammonia in ordinary phosphoric acid to a hot solution of sulphate of magnesia. The second, having the following composition, is of most importance:—

$$NH_3\ HO + 2MgO)PO_5 + 6HO.$$

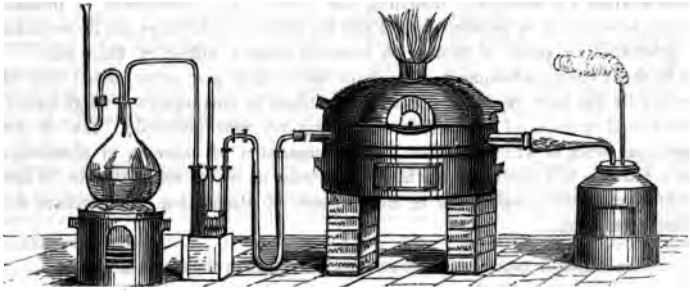
It may be generated by adding, firstly, solution of sal ammoniac, then ammonia, to a solution of sulphate of magnesia. The salt which deposits is completely insoluble in the generating fluids, and hence affords a ready means of separating magnesia from other bodies in analytical researches. The precipitate, however, is somewhat soluble in water, for which reason the filter containing it must be washed with the smallest practical quantity of that liquid, or still better, with a solution of sal ammoniac, in which the precipitate is insoluble. This double phosphate of magnesia and ammonia is occasionally found as the constituent of certain human urinary calculi.

Silicates of Magnesia.—Various silicates of magnesia occur naturally. Meerschaum, talc, and serpentine are familiar examples. Magnesian minerals are characterised by giving the impression of soapiness when touched.

Magnesium and Chlorine.—Chloride of Magnesium. Only one compound of these elements is known. It derives a certain interest as being the material employed for the production of magnesium.

Preparation.—When magnesia, its carbonate, or its hydrate, is added to hydrochloric acid until saturation of the latter has been effected, and the resulting solution

is carefully evaporated, a crystalline mass results, which is analogous, in its general nature, to crystallized chlorine of calcium. Theoretically, we might infer that the crystals in question should yield, when heated to the required extent, anhydrous chloride of magnesium—practically, however, the latter body cannot be obtained in this manner; it suffers decomposition, evolves hydrochloric acid, and leaves magnesia. Chloride of magnesium, however, may be obtained pure and anhydrous in the following manner:—Add sal ammoniac to a concentrated solution of magnesia in hydrochloric acid, and evaporate the mixture to dryness. Place the dried result in a platinum crucible, and heat the latter to redness. The fixed and fused result is pure chloride of magnesium.



General Characteristics distinctive of Magnesian Solutions.—They yield a white, gelatinous precipitate, with alkaline carbonates.

They yield a white precipitate with ammonia in solution, perfectly neutral, and free from ammoniacal salts. If the latter be present, however, precipitation of ammonia does not occur.

They yield a precipitate with lime-water.

They do not yield a precipitate with sulphuric acid, or sulphates, except their solutions be exceedingly strong.

Evaporated to dryness, the residue, moistened with nitrate of cobalt, and heated in a blowpipe flame, a rose-coloured tinge is produced.

ALUMINIUM.

Equivalent or atomic weight	13·7
Specific gravity	2·6

This metal is an extensive constituent of the inorganic world. It enters largely into clays and marls, and few rocks, understanding that term in the geological sense, are without it.

Preparation.—Aluminium may be prepared by decomposing chloride of aluminium by means of potassium or sodium, and washing away the resulting alkaline chloride with water; in which liquid aluminium is unalterable at any temperature.

Until lately aluminium had only been prepared in small quantities, and was but little studied; within the last year, however, a process for manufacturing it on the large scale has been instituted, under the auspices of the Emperor of the French, by M. St. Claire Deville. Several bars of aluminium have now been produced, and some

notions formerly entertained respecting it have been discovered erroneous. For example, the impression was formerly entertained that aluminium could scarcely be fused by the strongest furnace heats, whereas it is now found to melt with almost the facility of silver. Formerly, too, it was believed that aluminium would tarnish by exposure to watery vapour and general atmospheric influences; that notion, too, has been found incorrect.

The method of producing aluminium by M. St. Claire Deville is essentially the method formerly known—namely, by the action of sodium on chloride of aluminium. Potassium would have equally answered the purpose, as we have seen, had considerations of economy not interfered with its extensive application. Hitherto no method has been devised for materially lessening the cost of the production of potassium; sodium is, however, now procurable at Paris for about ten shillings per lb. avoirdupois. It is generated, in point of fact, with scarcely greater difficulty than zinc. It is owing to the extreme cheapness of sodium more than any other reason that M. St. Claire Deville has been enabled to obtain aluminium in comparatively large quantities, for his actual process of manufacture involves no new principle. He at present employs iron tubes in which to effect the decomposition of chloride of aluminium by sodium; but this is a contrivance which he informs us leaves something to be desired. Chloride of aluminium employed in the process of aluminium manufacture will be described farther on.

ALUMINIUM WITH OXYGEN—OXIDE OF ALUMINIUM OR ALUMINA.

The only known compound of aluminium with oxygen is alumina.

Preparation.—(1). By the addition of carbonate of ammonia to alum.

(2). By strongly heating ammoniacal alum.

Properties.—A white powder, insoluble in water, easily dissolved by a solution of potash, soda, strontia, or baryta, except it have been heated to redness, when its solubility in these agents is destroyed. Ammonia dissolves it also to a trifling extent. It is soluble also in acids to a large extent, if it has been recently thrown down, but slightly if it has been consolidated by heating. Alumina, coloured with various calcigenous metallic bodies, is found crystalline in nature, forming beautiful gems, of which the ruby and the sapphire may be cited as examples.

Considerable difference of opinion has existed amongst chemists as to the atomic constitution of alumina. Being the only known compound of aluminium and oxygen it might be inferred to contain a single atom of each. This assumption is, however, not believed to accord with the truth. Alumina is considered to be a compound of Al_2O_3. The percentage composition of alumina is as follows:—

Aluminium	53·27
Oxygen	46·73
	100·00

CHLORINE AND ALUMINIUM—CHLORIDE OF ALUMINIUM.

Alumina readily dissolves in hydrochloric acid; but chloride of aluminium cannot be obtained by evaporating the solution to dryness. When thus treated, a similar decomposition takes place to that already described under the head of chloride of magnesium.

Preparation.—Freshly precipitated alumina is intimately mixed with some highly carbonaceous substance, such as charcoal powder, sugar, tar, &c., and the whole made

into a paste with oil, if it have not the necessary consistence without. The mixture is next formed into pellets, which are to be dried, and strongly calcined in a crucible. These pellets being thrust into a porcelain tube run through a lighted furnace, and dried chlorine gas transmitted, chloride of aluminium passes over, and may be condensed into a crystalline mass by applying cold externally to the receiver.

Properties.—A straw-coloured body, solid and crystalline at ordinary temperatures; very prone to combine with water, from which, when once united, it cannot be separated by any known means.

ALUMINA AND SULPHURIC ACID (SULPHATE OF ALUMINA).

Preparation.—By saturating dilute sulphuric acid with freshly-precipitated hydrate of alumina (alumina plus water), and evaporating the solution.

Properties.—Crystallizes with difficulty in thin plates; soluble in twice its weight of water at 60° Fah. It affects litmus paper like an acid, and possesses a sweet and somewhat astringent taste. By a red heat it is decomposed, alumina being left. The alumina thus generated, however, is liable to be contaminated with a small portion of sulphuric acid.

Perhaps the most remarkable, and certainly the most important, property of sulphate of alumina is its tendency to unite with a second sulphate, and generate for each secondary combination a double salt. For example, there is a compound of sulphate of alumina and sulphate of potash; another compound of sulphate of alumina and sulphate of soda; a third of sulphate of alumina and sulphate of iron; a fourth of sulphate of alumina and sulphate of ammonia. To all the double sulphates in question the generic name of *alum* is applied. In this way we have potash alum (which is the salt commonly termed alum), soda alum, iron alum, ammonia alum, and some others. The atomic constitution of potash alum is as follows:—

$$Al_2\,O_3,\ 3SO_3 + KO,\ SO_3 + 24HO.$$

It is a salt of great importance in the arts, and is extensively manufactured on a very large scale. The raw material employed in the alum manufacture is *alum slate*, or *alum clay*, as it is sometimes termed. Alum slate is a compound or mixture of alumina, silica, and bisulphuret of iron. This being roasted, and exposed to air and moisture, it speedily disintegrates into powder. By this treatment the bisulphuret of iron becomes transformed into the monosulphate of that metal, and the alumina into sulphate of alumina. The solution being concentrated, chloride of potassium is added; by which treatment protochloride of iron and sulphate of potash result. The latter combining with sulphate of alumina, alum is generated in a solution of protochloride of iron. The latter material is very soluble, and does not crystallize readily; whereas alum can be crystallized by evaporation without difficulty. Hence this substance may be freed from the solution of chloride of iron by taking advantage of the property in question. In order to be pure, however, it requires to be redissolved and recrystallized, once at least, if not twice or more. For many purposes to which alum is applied in the arts, the presence of iron would be a disadvantage. Roman alum, generated by the natural decomposition of felspar, is celebrated for its complete freedom from iron, a quality which used to render it valuable; but since improved methods of chemical treatment have been adopted, alum prepared by artificial processes is turned out remarkably pure.

Potash alum crystallizes in forms, usually octohedral, belonging to the tessular or cubic system of Weiss and Mohs. It has a peculiar astringent taste, and manifests an

acid reaction on test-paper. It is soluble in its own weight of boiling water, and in 18 parts of water at 60° Fah. Burnt alum is the result of heating potash alum until all its water has been expelled. Exposed to a still higher temperature, sulphuric acid is evolved and the salt is decomposed.

Soda alum may be prepared like potash alum, by substituting chloride of sodium for chloride of potassium in the process of manufacture. It resembles potash alum in crystalline figure, taste, and general properties.

Ammonia alum is very similar to potash alum in all its physical and many of its chemical qualities. When strongly heated it is decomposed, the sole fixed result being alumina, if the operation have been conducted with adequate care. It is liable, however, to retain a little sulphuric acid; and for this reason the alumina resulting from this mode of treatment cannot be relied upon for extreme purity.

Distinctive characteristics of Aluminium Compounds in Solution.—They all yield a precipitate with ammonia. Solutions of caustic potash and soda yield a precipitate soluble in excess of the precipitating agent. They are precipitated by lime-water, also by alkaline carbonates—not, however, as carbonate of alumina, but as the hydrate of that earth, also by alkaline hydrosulphates.

Mixed with nitrate of cobalt, and heated in the blow-pipe jet, a blue colour is developed.

GLUCINUM OR GLUCINIUM, THORIUM, ZIRCONIUM, YTTRIUM, ERBIUM, AND TERBIUM, CERIUM, LANTHANIUM, AND DIDYMIUM.

These metals are so exceedingly rare, and so seldom enter into the ordinary routine of chemical inquiries that an elaborate description of them is unnecessary here. They constitute the respective metallic radicles of oxides which are earths, and are designated by changing the final *um* of the respective metals into *a*. Like aluminium and magnesium, the respective chlorides of the metals in question, yield up their chlorine when treated in close vessels with potassium or sodium. The oxide of glucinium, or glucina, exists naturally in several minerals, chiefly varieties of the emerald, which substance may be regarded as a double silicate of alumina and glucina. Glucina resembles alumina in its general properties, but it differs from that earth by its capability of dissolving in solution of carbonate of ammonia, also by the sweetish taste possessed by its soluble compounds; hence the terms *glucinium* and *glucina*, from γλυκυς, sweet. Glucina does not, like alumina, form alums, nor does it yield a blue colour when mixed with nitrate of cobalt, and heated in the blow-pipe flame. Zirconia (*oxide of zirconium*) derives its name from the mineral termed *zircon:* it is a silicate of zirconia, $2Zr_2\,O_3$, $Si\,O_3$ generally mixed with small amounts of oxide of iron. Zirconia is precipitated by caustic fixed alkalies, but does not dissolve in an excess of the precipitant,—a characteristic by which it may be distinguished from alumina and glucina. *Thorina* (oxide of thorium) was discovered by Berzelius. Only two minerals, *thorite* and *pyrochlore*, both very rare, are known to contain it. Thorina is perhaps the heaviest compound in nature, with the exception of metallic alloys—its specific gravity being no less than 9·4. Its sulphate has the rare quality of being more soluble in cold than in boiling water. *Yttrium*, *erbium*, and *terbium* are found respectively in the three rare minerals *gadolonite*, *æthite*, and *yttrotantalite*. *Cerium*, *lanthanium*, and *didymium* are found associated in several minerals, but most especially in the mineral known as cerite.

CERAMIC WARE—POTTERY AND PORCELAIN.

Having discussed the properties of kaligenous and terrigenous metals, it is now time to enter upon the consideration of the series of remarkable compounds, or rather a mixture of the compounds, which in the aggregate form the various descriptions of ceramic or potters' ware. The term ceramic, in its generic sense, applies to the materials of the potter's art; it has reference to compounds of very different value, from the low-priced brick to the costly productions of Sèvres, Dresden, China, and Japan.

General Remarks.—Few nations, whether savage or civilized, have been without some kinds of ceramic ware. Vessels of this material are found in the islands of the South Sea: they were manufactured by the ancient Aztecs. The ancient Greeks and Romans brought the manufacture to a high degree of excellence, though they never appear to have progressed so far as the Assyrians and Babylonians. The manufacture, however, of the greatest triumph of ceramic art, *porcelain*, was, until late times, a secret known only to the inhabitants of China and Japan. Much difference of opinion still exists as to whether specimens of real porcelain were ever seen by the ancient Greeks and Romans. Some authors maintain the affirmative, and believe that the so called Murrhine Vases, concerning which we read in Roman authors, were nothing else than specimens of real Oriental porcelain. I am disposed, however, to think, taking all the circumstances of the case into consideration, that they were not of porcelain, and that the opinion of Dr. Thompson, who assumes them to have been vases of Derbyshire spar, was correct. In a manual of non-applied chemistry, such as this, no detailed account of the numerous varieties of ceramic ware can be offered. The following general principles will, however, give the reader an insight into the nature of these productions.

Alumina is amongst the most infusible of compounds, but when combined with silica (silicic acid), as we find it in clay, and more especially when combined with oxide of iron, and of other calcigenous metals, or with the fixed alkalies—its degree of fusibility is increased. Hence clays naturally existing are more or less refractory in the fire, the degree of their refractoriness being in proportion as the total amount of alumina predominates. By taking advantage, then, of this circumstance, the ceramic manufacturer has it in his power to produce fictile materials which shall be capable of almost any degree of igneous agglomeration up to the point of complete fusion; when the result ceases to be pottery in any sense, and becomes glass.

Now, pure alumina, or a mixture of alumina with silica, or of these with the fixed alkalies, may be exposed to any degree of heat without suffering any diminution of their whiteness; but if oxide of iron should happen to be present, as is usually the case in most natural clays, the result will be coloured more or less red, as we find in bricks and tiles. It follows, therefore, that white ceramic ware only admits of being prepared by one of two methods: either by utilizing materials naturally existing, or by forming these materials artificially. The latter case involves a somewhat advanced acquaintance with chemical principles, hence the manufacture of white ceramic ware was long confined to privileged localities, and the best description of white ceramic ware (real porcelain) was long a monopoly of China and Japan.

Coloured Ceramic ware.—Familiar examples of these are seen in our modern bricks and tiles, but it was brought to the highest degree of perfection by the Greeks anterior to the time of Alexander the Great; also by the Etruscans. The latter people chiefly excelled in the manufacture of coffins made of this material, and the Samian Greeks in the manufacture of vases.

Ancient classic vases are of two kinds—plain and ornamented. Of the latter, again, there are two distinct varieties—red ornamentation on black ground, and black ornamentation on red ground. Both varieties of ornamental vases were much prized, and seem to have been only employed for religious uses. Their manufacture had arrived at its highest degree of excellence at a period anterior to the sway of Alexander the Great. This conqueror was the first to introduce into Greece the gold and silver vessels, which diminished the value of ornamental ceramic vases, and caused their manufacture to languish, and eventually to be discontinued. In the time of Augustus they had already begun to be spoken of as ancient vases, to be sought in tombs and treasured in museums, just as moderns do now.

White Ceramic ware.—It is a subject of deep regret that the classic nations were limited in their ceramic productions by the nature of the material at their disposal. They had only clays which would burn red; therefore, when they had fashioned them into elegant forms, and painted these with black figures, their resources of ceramic ornamentation were exhausted. Two practical means of surmounting this difficulty are alone possible,—either coloured ceramic ware must be overlaid with a white opaque varnish, or enamel, or the body of the material must be white; neither resource was possible to the ancient Greeks and Romans, though, as will appear in the sequel, the former expedient was known to the Assyrians and Babylonians. Objection may be taken to the classification of red pottery, white-enamelled, with white ceramic ware; nevertheless, for convenience of general classification, that scheme may be adopted.

Red Pottery white-enamelled (Majolica ware).—The term majolica is derived from Majorca, the locality in which the variety of pottery under consideration was first established by the Spanish Saracens, amongst whom it was brought to a high degree of excellence; subsequently the same kind of material was manufactured in Italy, and some of the greatest Italian artists were employed in embellishing it with their designs. Italian majolica, however, is not valued so highly amongst dealers as the real Moorish majolica. The principle on which the construction of majolica ware is based is simply this:—common red pottery being unadapted to give effect to chromatic ornamentation, its surface is covered with an opaque enamel, chiefly composed of oxide of tin, which totally conceals the underlying material, and gives the painter full scope for his designs. Of this kind are the *azulejos* or coloured tiles, found in the Alhambra, and other Moorish constructions. It is commonly thought that the Saracens invented this beautiful ware; but the recent discovery of a tin-enamelled tile, ornamented with paintings, in the ruins of Nineveh, diminishes the probability of the assumption. It is by no means unlikely that the secret lingered in some Asiatic recess, and was learned by the Arabs before their irruption into Europe.

Porcelain.—Of this material two distinct kinds are recognised—hard and soft porcelain. To the former belong the white ceramic productions of China, and Japan, Dresden, and New Sèvres; to the latter the wares of Old Sèvres, Madrid, Chelsea, Bow, and some other localities. The distinction, however, is more arbitrary than is commonly imagined.

We have already seen that in proportion as silica, alkalies, and calcigenous acids enter into the composition of pottery, so is it rendered more fusible and more soft. Theoretically, therefore, the limits between hard and soft porcelain should not be well defined. Practice confirms theory in this respect. The white ceramic wares of China and Japan have been considered the type of true or hard porcelain. Nevertheless, M. Ebelmen and others have satisfactorily demonstrated that it is less hard than the

productions of Sèvres at the present time; in point of fact, the Chinese add portions of potash to their silicated paste, which European manufacturers of porcelain do not. The sort of potash employed for this purpose amongst the Chinese is fern ashes. The materials employed by the Chinese in their porcelain manufacture strictly conform with chemical requirements. The aluminous staple is furnished by decomposed felspar, and is called by the natives *kaolin*; the siliceous material is known by them as *petunse*. The Dresden, or rather Meissen porcelain, is manufactured from a bed of clay naturally existing, which needs no siliceous admixture.

Soft Porcelain.—Before the chemical constitution of hard or oriental porcelain was understood, and the materials for making it in Europe rendered available, various fictitious pastes took its place. They differed in their constitution in different manufactories; but they all consisted of white clay, mixed with materials having the property of ready fusibility, such as powdered glass, borax, oxide of lead, &c. By this admixture the natural tenacity of clay, rendering it so valuable to the potter, enabling it to be readily turned wet on the wheel and moulded into forms, was lost. Other adventitious mixtures were rendered necessary, such as size, soap, &c., to impart the necessary tenacity. Notwithstanding all this preparation, vessels of soft porcelain could not be completely finished wet; they had to be turned dry, and this was an operation very detrimental to the workmens' health. This manufacture has now disappeared.

Faïence or Earthenware.—The term porcelain, or chinaware, is usually restricted to the material which is semi-transparent, and breaks with a conchoidal fracture. Both hard and soft porcelain, though different as to chemical composition, agree in this respect; but our Staffordshire ware, which is universally admitted to be the finest description of earthenware, is opaque, and the conchoidal character of fracture is in it wanting. The chief peculiarity of this material consists in having a portion of bone-earth intimately mixed with the siliceous and aluminous materials, properly constituting a ceramic material. The presence of this bone-earth adds to the quality of whiteness, and produces the due amount of semi-fusibility. Staffordshire ware is not equal in beauty to porcelain, either hard or soft, but it is less expensive than either, and combines in an eminent degree the qualities of beauty and utility; services of it are therefore, better than any other ceramic matter, adapted to our ordinary wants, and our native manufacturers see with pride their productions dispersed over every part of the known world. The African negro princes obtain English wash-basins at an immense cost and risk, by caravan travelling over the Sahara, to be used as soup-basins; and the inhabitants of France and Germany—the very cradles of the European porcelain manufacture—never think their cupboards properly furnished until a service of Staffordshire ware is seen on its shelves.

Stoneware.—This material has also, like the preceding, been brought by us to a greater degree of excellence than elsewhere. The so-called Wedgewood ware is of this kind, and is the best of its class.

Parian Ware.—This exceedingly beautiful material, much employed at present in the manufacture of statuettes, vases, and breakfast-services, is a ceramic material, rendered very fusible by admixture of borax.

Glazing.—Most kinds of pottery are now glazed, and the glazing material is subject to variation. The chemical principles required to be taken cognizance of in the operation of glazing is to produce a glaze with a degree of fusibility commensurate with that of the body on which it is laid, and which, after cooling, shall have a propor-

tionate expansive and contractile rate. We very often see the glaze on articles of crockery ware cracked and disintegrating,—results which flow from a violation of the principles indicated. Hard porcelain being the most infusible variety of ceramic ware, the glaze adapted for it should have the same quality. Powdered felspar, a native silicate of alumina, and potash, is that which answers the purpose better than any other. Soft porcelain, and English Staffordshire ware, however, will not stand the necessary degree of heat to cause the glaze to fuse, hence its fusibility is augmented by the addition of borax and oxide of lead. In proportion as the two latter materials predominate, so does the glaze increase in fusibility, and, what is very disadvantageous, in *solubility*. The lead glaze of common earthenware is easily removed by the action of both acids and alkalies, and thus becomes a source of insidious lead poisoning.

The Lambeth stone ware, and some other kinds are glazed by a thin, but hard and totally unobjectionable varnish of silicate of soda. Technically this is known by the appellation of "*salt glaze*," from the method of imparting it, which is as follows:—whilst the stoneware is yet glowing in the furnace, a door is opened, and common salt (chloride of sodium) is thrown in. Silicic acid, at elevated temperatures decomposes chloride of sodium, chlorine being evolved, and silicate of soda formed. This result is attributable to the fixed nature of silicic acid at high temperatures, and the volatility of chlorine.

Coloured Ornamentation of Ceramic ware.—The pigments employed in this operation are necessarily mineral. Preparations of cobalt furnish us with blue, copper with greens and blacks, manganese with black, cobalt with pink, iron with black and red, whilst gold and platinum—rarely silver—are employed to impart their several metallic lustres. The principles involved in ceramic ornamentation by pigments, are of two kinds, either the pigment is incorporated with the original material, or it is laid on by a process similar to that of enamelling. In the production of porcelain in China and Japan, enamel, or *muffle* colours, as the French term them, are scarcely employed; but European manufacturers, aiming as they do at a higher style of artistic effect, rely upon the muffle for all their delicate gradations of colour.

Glass.—This material, considered in a technological sense, may be described as an alkaline silicate, or a mixture of alkaline with earthy silicates, and in some cases calcigeno-metallic-silicates, fused to the condition of pastiness, and allowed to consolidate. Glass therefore, chemically considered, bears a near relation to ceramic ware, especially the variety known as *soft porcelain*. The kinds of glass employed in the arts and manufactures are very numerous; they admit, however, of division into the three kinds of colourless glass without lead; colourless glass with lead (termed by us flint-glass, but crystal by the French), and lastly, the various varieties of coloured glass. As glass of these three divisions, and all their several varieties, is composed of an alkaline-silicate, or silicates, as a basis, it will be necessary to commence our description of glass by the consideration of this class of chemical bodies.

Silicates of Alkalies.—Silicic acid, or silica, readily combines with alkalies when fused with them, or with their carbonates; in the latter case carbonic acid being evolved. Apparently the combination takes place in all proportions; but this seeming infringement of the laws of definite combination, may be explained by assuming that a limited number of chemical silicates results, but give rise to the idea of illimitability by admixture with each other.

Whatever be the ratio in which silicic acid stands to the alkali, the fused results agree in certain general qualities. They are all transparent, more or less; they all,

when heated, sufficiently assume the condition of pastiness before that of perfect liquidity; they all break with a conchoidal fracture. They differ, however, so greatly in their relative degree of solubility in water and acids, that whilst the ordinary variety of glass employed seems to be absolutely insoluble in these agents, other kinds of glass may be prepared so exceedingly soluble in water that they may be employed as a substitute for starch in imparting stiffness to linen, on which it confers the quality of incombustibility, under all ordinary circumstances to which dresses are likely to be exposed.

Soluble glass of this kind may be prepared by carefully incorporating one part of silicic acid (powdered silver-sand answers perfectly well) with not less than three or four parts of carbonate of potash or soda, and exposing the whole to a strong red heat until the mixture has perfectly fused and carbonic acid has ceased to escape. Glass of this kind is perfectly soluble in water; but on adding a sufficient quantity of almost any acid, the silicic acid is precipitated in a gelatinous condition. The generation of varieties of this soluble glass is of frequent occurrence in the laboratory of research, constituting, as it does, the first step in many kinds of mineral analysis.

In proportion as the amount of alkali is made to decrease, so does the resulting glass assume the condition of greater insolubility; it would be incorrect, however, to say that any glass is absolutely insoluble in water. Powdered glass is dissolved to some extent in water of ordinary temperature, and glass in masses can be dissolved by exposing it to the prolonged action of water heated under pressure, as in the boiler of a high pressure steam-engine for example.

The most valuable quality of silicates of alkalies considered as glass-making materials has already been adverted to; they all, before entering into perfect fusion, assume the condition of intermediate pastiness so favourable to the requisitions of the glass-blower. This quality they preserve moreover when fused with other silicates, either of the terrigenous or the calcigenous class. Considered with reference to the kind of alkali employed, glass admits of division into soda glass and potash glass. The former is, perhaps, more generally eligible for all common purposes, though potash glass is less subject to crack on exposure to mutations of heat and cold, and therefore best adapted for chemical purposes. Bohemian glass is of this kind.

As regards the various manipulative processes for fashioning glass into shape, a manual of this kind can take no extended cognizance of them. They will be discussed in the treatise on chemistry applied to the arts and manufactures. It must suffice to indicate that flat glass is produced either by one of two varieties of glass-blowing, or by casting on a highly polished bed and subsequently grinding its surfaces even.

Common window glass is produced by the two first operations, whilst plate glass, employed for the better sorts of mirrors and for the glazing of high-priced windows, is produced by the last. Glass vessels are either produced by the operations of blowing and modelling, or blowing and moulding, the more expensive kinds of vessels being formed by the subsequent operation of cutting on a wheel.

Practically glass is never made for technological purposes with an alkali and silica alone; certain other silicates being invariably present. The silicates of lime, magnesia, and alumina, mixed or severally, diminish the fusibility of glass without adding to its colour; but silicates of the calcigenous metals, those of lead and a few others excepted, all have the property of imparting colour to glass, and are to this end employed. Oxide of lead being mixed with the materials of ordinary white glass increases their fusibility and adds to the luminous refrangibility, and accordingly to the lustre of the

resulting materials—hence the appellation *crystal*, as applied to glass of this kind by the French, is intelligible enough, whereas our expression, flint glass, as applied to the same, is altogether unmeaning. Good English flint glass, according to Faraday, is composed as follows:—

Silica	51·93
Potash	13·77
Oxide of lead	33·28
	98·98

Coloured Glasses.—Various processes are adopted for producing this beautiful material, such as those of staining enamelling or painting, and their various combinations. By stained glass is understood the material coloured throughout by the incorporation of a coloured substance, necessarily metallic, with white glass. Glass enamelling, or painting, involves the laying on of colours with a brush, and subsequently exposing the glass thus treated to the heat of an enamelling furnace.

Red colours are imparted to glass by means of preparations of copper and of gold. Cobalt yields blues; manganese oxide, amethyst; preparations of arsenic and tin, dead white; black oxide of copper yields greens, and iron compounds greens or browns. Metallic gold and platinum are sometimes employed to impart to glass their characteristic lustres.

Calcigenous Metals.—Hitherto our attention has been devoted to metals, the oxides of which are alkalies or earths; we now enter upon the consideration of metals, the oxides of which were termed by ancient chemists *calces*, and which are, therefore, known as the *calcigenous metals*.

MANGANESE.

Equivalent or atomic weight	27·6
Specific gravity	about 8

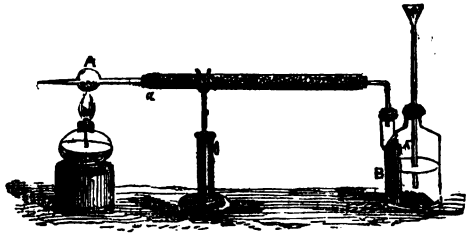
Preparation.—Although manganese ores are common, the metal itself is merely produced in small quantities as a chemical curiosity, by subjecting a mixture of oxide of manganese and carbonaceous matter to a very high temperature in a closed crucible. Protoxide of manganese is first generated by calcining carbonate of manganese in a crucible. The resulting protoxide is then incorporated with one-tenth its weight of charcoal powder, and a little fused borax. This mixture is rammed into a crucible lined with charcoal, covered, and exposed to the highest heat of a smith's forge. The result is not pure manganese, but a carburet of that metal, standing, therefore, in the same relation to manganese, that cast does to wrought iron. Its purification may be effected by mixing it with carbonate of manganese, and heating it a second time in a well-covered porcelain crucible, enclosed within a Hessian or Cornish crucible.

Properties.—Something like iron in general appearance, but more brittle, and somewhat more difficult to fuse. Manganese rapidly tarnishes by exposure to air, crumbling down to oxide. It decomposes boiling water with rapidity, hydrogen being evolved; and can only be preserved for long periods by immersion in naphtha, like potassium and sodium, or by retaining it in an atmosphere of hydrogen or nitrogen gas.

Oxides of manganese.—Of these there are five primary and two secondary, the latter resulting from the combination of primary compounds with each other.

Protoxide of Manganese—(MnO).

Preparation.—Either by deoxidising, by means of hydrogen, the peroxide of manganese, or by calcining carbonate of magnesia without simultaneous atmospheric contact. This latter process may be effected, as described at page 434, by heating carbonate of manganese in a covered crucible, when the resulting protoxide is only slightly alterable by exposure to the air; or carbonate of manganese may be reduced in a tube of the following description :—



A is a glass bulb holding carbonate of manganese, *a* is a tube containing fragments of dried chloride of calcium, and B is a generating apparatus for liberating hydrogen gas. The latter of course passes dry over the carbonate of manganese in the bulb A, and displaces the air formerly there existing. So soon as this displacement has been totally effected, the flame of a spirit-lamp is applied to the glass bulb, carbonic acid gas is evolved from the carbonate of manganese within, and protoxide of manganese remains. Finally, each tubular extremity of the bulb being sealed, the oxide of manganese may be preserved for an indefinite period.

Protoxide of manganese readily combines with acids, generating protosalts, from solutions of which a white hydrate of the protoxide is thrown down by caustic potash and soda.

Sesquioxide of Manganese—(Mn_2O_3).

Preparation.—By exposing peroxide of manganese to red heat (as in the preparation of oxygen) until no more gas is expelled, and treating the fixed result by an acid, sesquioxide of manganese is left. It also occurs native, both hydrated and anhydrous.

Properties.—In physical appearance it somewhat resembles the black or peroxide of manganese, next to be described, but is more tawny red, or brown.

Binoxide or Peroxide of Manganese, MnO_2.—This is more common than any of the other oxides of manganese, being found native in considerable quantities, and sufficiently pure for employment in many industrial arts. The chief purpose for which peroxide of manganese is used is for the preparation of chlorine, as described when treating of that simple body. Peroxide of manganese combines with water to form a hydrate of definite composition. It may be generated either by transmitting chlorine through carbonate of manganese held suspended in water, or by pouring hot water on the manganate of potash.

Manganic Acid, MnO_3 and *Permanganic Acid*, Mn_2O_7.—Both these compounds may be generated by heating together a mixture of caustic potash with peroxide of manganese in the presence of oxidising bodies, such as chlorate or nitrate of potash. The residue of this operation when treated by water, and the liquid evaporated in vacuo, yields crystals of manganate of potash. If these crystals be treated with hot water, they are decomposed into hydrated peroxide of manganese, which precipitates, and solution of permanganate of potash, which is purple, remains. The crystals of man-

ganate of potash employed for this operation should not contain an excess of potash, otherwise the formation of permanganate does not satisfactorily take place. Permanganate of potash may also be prepared directly by the following process:—Peroxide of manganese and chlorate of potash are mixed in equal proportions; one part of hydrate of potash dissolved in the smallest available quantity of water is then added, the whole evaporated to dryness, and heated short of redness. Hot water being now poured upon the mass, permanganate of potash is dissolved out, and may be readily crystallized, whilst the insoluble oxide is separated by decantation, not by filtration, because both this and the preceding compound are decomposed by contact with organic bodies. *Manganic acid* has never yet been obtained in the state of isolation, but an aqueous solution of permanganic acid may be generated by the accurate decomposition of permanganate of baryta by means of sulphuric acid.

Red Oxide of Manganese Mn_3O_4, and *Varvicite* Mn_4O_7, are not separate oxides of manganese, but combinations of two oxides in the manner of acid and base. Red oxide is regarded as a compound of $MnO + Mn_2O_3$. It constitutes a native ore of manganese, and may be artificially generated by heating the protoxide or sesquioxide to whiteness, or by heating the carbonate of manganese to redness, in an uncovered vessel. It does not form salts, and when fused with borax or white glass, imparts an amethyst colour.

Varvicite, $Mn_2O_2 + 2MnO_2$.—So called because of the locality, *Warwickshire*, in which it was discovered and is principally found. In appearance it resembles the peroxide, than which it is more black; and it also contains water, being a hydrate.

Salts of Manganese.—The only oxygen compounds of manganese which act as bases to acids are the protoxide and the sesquioxide. The former yields a large number of well characterized stable salts; the latter, on the contrary, is a very feeble base, and its salts are all unstable. Respecting the characteristics of the manganates, and permanganates—salts in which the manganese compound performs the function of acidity—a few remarks have already been offered.

In almost every case of analysis, involving the solution and subsequent isolation of manganese, this metal will be found in the state of proto-combination,—either as an oxygen salt of the protoxide, or as a protohaloid salt; hence, to these the learner should direct his especial attention.

The first point to be especially remembered in connection with solutions of protosalts of manganese, and, indeed, the metal in any state of solution, is, that no precipitate or change of colour is yielded by hydrosulphuric acid. Now, manganese being a calcigenous metal, this absence of precipitate or change of colour is remarkable; only five calcigenous metals,—manganese, iron, uranium, cobalt, and nickel,—being thus circumstanced.

The second point to be remembered in connection with the chemical peculiarities of manganese is, that hydrosulphate of ammonia (sulphide of ammonium), yields a precipitate with the solutions above indicated, and the precipitate is of a light flesh colour. This, again, is a peculiarity; black being the usual tint produced by hydrosulphuric acid, or hydrosulphate of ammonia in metallic solutions.

Caustic potash or soda yield, with the solutions of manganese salts above specified, a white precipitate, rapidly changing to brown.

Soluble carbonates, especially those of the fixed alkalies and of ammonia, throw down a whitish carbonate of manganese, not liable to much change by exposure to the air, and from which other protosalts of manganese may be readily generated. Ferro-

cyanide of potassium also yields a white precipitate; and chlorine,—or materials which readily evolve chlorine, such as commercial chloride of soda, or of lime,—throw down the red oxide of manganese, by reason of their oxidising agency. In point of fact, a solution of chlorine, or of chloride of soda or lime, is one of the most delicate tests we possess for indicating and separating manganese. Manganese, when present, in whatever variety of combination, may be readily indicated by the blowpipe. When fused with borax in the external or oxidising flame, it yields a purple bead, which becomes colourless when removed to the internal flame.

IRON.

Equivalent or atomic weight	28
Specific gravity about	7·8

General Remarks.—This most important metal, though widely disseminated throughout the inorganic kingdom, and forming no inconsiderable constituent of animals, is seldom obtained pure. Fortunately, none of its various applications involve the necessity of having it quite pure, otherwise materials of iron, instead of being amongst the cheapest, would be amongst the most costly in existence.

Preparation.—Three processes may be indicated for yielding iron chemically pure. They are as follow :—

(1). Having tied some small iron wire in a bundle, place the latter in a porcelain tube, heat it to redness, and pass through a current of aqueous vapour. By this means the iron wire is covered with rust, which is the object designed. Next, cut this iron into short pieces, mix them with a little powdered glass, pack the mixture in a small porcelain crucible, bed the latter in another crucible of Hessian ware, and expose the whole to the strongest heat of a wind furnace. By this treatment, oxygen from the iron rust unites with the carbon and other impurities of the non-oxydised portion of the wire, leaving the remaining portion of iron pure. It aggregates, if the furnace-heat be sufficiently high, into one mass.

(2). Pure iron may also be obtained by transmitting hydrogen through oxide of iron contained in a tube and heated. The heat generated by a spirit lamp flame is amply sufficient for developing the result, and the little apparatus depicted at page 435 may be here employed. Iron, however, prepared at this low temperature, is pyrophoric: it burns immediately on coming in contact with air, and hence can only be preserved by hermetically sealing it in the tube employed for its preparation. If, instead of a glass tube, one of porcelain be employed, and the current of hydrogen transmitted at a furnace-heat, the resulting iron becomes more dense, loses its pyrophoric quality, and may be exposed to dry atmospheric air without change.

(3). The third method of obtaining pure iron, consists in substituting protochloride of iron for oxide of the metal. In this case iron is obtained, not in the condition of powder, but as a mirror-like scale.

Varieties of Commercial Iron.—The principal varieties of commercial iron are three —cast iron, wrought iron, and steel. Of each of these there are numerous sub-varieties, but they cannot be minutely detailed here.

Cast iron is a very heterogeneous compound, though it is generally regarded as a mere union of carbon with iron, the carbon being in greater quantity than necessary to form steel. Besides carbon, cast iron contains silicon—probably aluminium, sulphur, and occasionally phosphorus. By the presence of carbon and other adventitious

bodies, iron becomes more fusible than when pure; hence the propriety of the term "*cast iron.*"

By repeatedly fusing cast iron, and rolling and hammering the glowing mass, the greater portion of carbon and other collateral impurities are burned or otherwise removed, leaving the iron in the state of comparative purity. In general terms we may say that the more iron has been fused, hammered, drawn out, rolled or kneaded, the purer does it become: hence, iron wire is composed of very pure iron, and the purity of old horse-shoe nails is so well recognized that they sell at a comparatively high price, to be converted into gun barrels.

Steel.—This material is considered to be a carburet of iron, in which the proportion of carbon is less than the quantity requisite to constitute cast iron. The fine Indian variety of steel termed *wootz*, however, contains minute portions of aluminium as well as carbon, and it is doubtful whether any variety of steel be a mere combination of iron with carbon. The most usual plan adopted for the conversion of iron into steel is that of cementation, as it is called. Bars of wrought iron are stratified with charcoal, and exposed for a considerable period to a high furnace temperature, when union between iron and carbon takes place, steel being the result.

Iron approaching the condition of purity, such as wrought iron and steel, is endowed with the valuable quality of welding—that is to say, two pieces of wrought iron or steel being taken and heated to whiteness in a forge, they may be caused to adhere by hammering. In this respect iron, amongst all the calcigenous group of metals, furnishes the only perfect example. Platinum is described as participating in the quality of welding, but its capabilities in this respect are very slight. The kaligenous metals, potassium and sodium, it may be remembered, readily admit of welding.

Oxides of Iron.—Four compounds of iron with oxygen are known as follows:—

	Iron.	Oxygen.
Protoxide	1	1
Sesquioxide (peroxide) . . .	2	3
Black oxide	3	4
Ferric acid	1	3

Protoxide.—FeO. This is the only oxide of iron having the properties of a strong base, and yielding well-defined crystalline salts.

Preparation.—By adding caustic potash, soda, or ammonia, to any salt of the protoxide, the latter is precipitated in the form of a greenish-white hydrate, and which by boiling, assumes the colour of almost perfect blackness. The protoxide of iron is exceedingly difficult to retain unchanged. Exposed to the air, or any gas containing oxygen, it soon becomes green, then red-brown, the latter tint being indicative of the change to peroxide. Most of the common salts of protoxide of iron are green when pure, but, exposed to oxydising influences, they become covered with a layer of red material—peroxide combined with the original acid. All protosalts of iron are readily converted into persalts by boiling with nitric, or with nitrohydrochloric acid.

Peroxide of Iron, Fe_2O_3.—This is also a basic substance, but not powerfully so. In its relations it resembles alumina.

Preparation.—When a protosalt of iron is boiled with nitric or nitrohydrochloric acid, a persalt of iron results; from the solution of which peroxide of iron may be precipitated by ammonia. It also occurs native in the Island of Elba and elsewhere, constituting the ore known as specular iron. Hydrate of the peroxide is also found native, constituting the ores known as hæmatites, red and brown.

Properties.—Peroxide of iron has a full blood-red colour. It is not affected by any degree of heat, except carbon or other deoxidising agent be present; when it is reduced to the condition of metallic iron. This oxide of iron is not magnetic.

Black, or Magnetic Oxide of Iron, Fe_3O_4.—This, when found native, constitutes the loadstone, so called from its magnetic properties.

Preparation.—The black scales which form on wrought iron when heated to whiteness, as in the operation of forging, are chiefly composed of this oxide. It may also be prepared in the moist way by effecting a mixed solutionof a proto and a persalt of iron, precipitating the solution by an alkali and boiling the hydrates which deposit. A black crystalline compound forms and precipitates; it is the oxide in question.

Ferric Acid—(FeO_3).

Preparation.—Four parts of nitre and one part of peroxide of iron are to be intimately mixed and heated to redness in a covered crucible. The contents, being allowed to grow cold, then dissolved in water in which ice is melting, and consequently the temperature of which is at 32° F., a solution of ferrate of potash is obtained. This compound is remarkably prone to decomposition, oxygen gas being evolved and peroxide of iron thrown down. The change takes place slowly in the cold, but hot water occasions it at once. Ferric acid yields a remarkable and very permanent compound with baryta. In colour it is a deep crimson, and may be used advantageously as a pigment.

Chlorides of Iron.—Of these two are known, the protochloride and the sesqui or perchloride.

Protochloride of Iron—(Fe Cl).

Preparation.—By passing a stream of dry hydrochloric acid gas over red-hot iron contained in a tube of porcelain, or by dissolving iron in hydrochloric acid.

Properties.—A brown fixed material, which, when obtained in the dry way, furnishes crystals on cooling. The solution of iron in hydrochloric acid, when evaporated, yields green crystals of the hydrated protochloride, having the composition of $FeCl + 6HO$.

Sesquichloride of Iron—(Fe_2Cl_3).

Preparation.—By passing a current of dry chlorine gas over iron heated to redness, and subliming the resulting chloride in an atmosphere of the same gas, or by dissolving iron in nitrohydrochloric acid.

Properties.—An iridescent brown or greenish-brown compound, soluble in alcohol, ether, and water. Its solutions are decomposed by light, sesquioxide of iron being deposited. By evaporating the solution of iron in nitrohydrochloric acid, crystals of the hydrate of the sesquichloride are produced; they dissolve in water, alcohol, and ether, and are very deliquescent. If aqueous solution of sesquichloride of iron be evaporated to dryness and sharply heated, partial decomposition ensues, peroxide and hydrochloric acid being simultaneously formed. The portion of chloride remaining undecomposed sublimes in red and very deliquescent crystals.

Iron with Sulphur.—Many compounds of iron with sulphur exist, but two only have been well studied; they are the protosulphuret and the bisulphuret.

Protosulphuret of Iron—(FeS).

Preparation.—By heating a bar of iron to whiteness, and bringing it into contact with sulphur, or by heating a mixture of 2½ parts of sulphur and 4 parts of iron filings

in a red-hot crucible. This is the compound employed in laboratories for generating hydrosulphuric acid.

Bisulphuret of Iron—(FeS_2).

This compound, as will be seen, corresponds to no known iron oxide; it exists in nature, constituting iron pyrites, and may be formed artificially by mixing 2 parts of protosulphuret of iron with 1 of sulphur, and heating the mixture in a crucible until all excess of sulphur has been expelled. When heated, the bisulphuret of iron evolves a portion of its sulphur, and the material which remains is composed of 68 per cent. only of sulphur, in combination with 32 of iron. The exact atomic composition of this compound is not known.

There is also found native a mineral termed *magnetic pyrites*, the composition of which is indicated by the formula Fe_7S_8; it is probably a compound of $5FeS + Fe_2S_3$.

Combinations of Iron with Phosphorus.—Phosphorus unites with iron in many proportions. The phosphuret best known is that generated by heating in a crucible lined with charcoal, a mixture of phosphate of iron and charcoal powder. The presence of phosphorus in iron is very detrimental, imparting to it the quality known as *cold short*,—that is to say, iron thus contaminated is very brittle, and when cold, readily crumbles under the stroke of the hammer.

Iron with Nitrogen.—A compound of this kind is known, but its atomic composition has not been determined. It may be prepared either by passing dry ammoniacal gas over iron wire heated to redness in a porcelain tube, or exposing anhydrous protochloride of iron contained in a glass tube to a heated current of dry ammoniacal gas.

Iron with Cyanogen.—Cyanogen, throughout the whole range of chemistry, is characterized by the number and the complexity of its compounds. This remark especially applies to the cyanurets, or cyanides, of iron, of which there are several. Under the head of cyanogen (page 391) the circumstance was mentioned, that although a compound it acted like a simple body. This peculiarity is also retained by the compounds of cyanogen with other bodies;—thus, for example, cyanogen unites with protoxide of iron to form cyanide of iron, and the latter unites again with other cyanides, such as potassium, lead, &c., constituting double cyanides. Of this latter class of bodies, the most important not only as regards its uses, but as furnishing a key to the comprehension of all the remaining double cyanides is the double cyanide of iron, and potassium, the yellow prussiate of potash, as it is commonly designated.

Protocyanuret of Iron.

Preparation.—(1). By adding a solution of cyanide of potassium to a solution of any protosalt of iron. Proto-cyanuret of iron, as thus made, retains portions of cyanide of iron so obstinately, that it can scarcely be got pure by this process, even after the most assiduous washing.

(2). By digesting Prussian Blue with a solution of hydro-sulphuric acid.

Properties.—A white compound, rapidly becoming blue when exposed to the air.

We have already seen that cyanogen, though a compound body, assimilates itself by chemical relations and demeanour to chlorine, iodine, and bromine. Like them it combines with hydrogen to form a hydracid (the hydro-cyanic); like them it unites with certain metals, forming compounds which necessarily must be regarded as cyanides, and not hydro-cyanates, seeing that they contain neither oxygen nor hydrogen. In fact, all the remarks relative to hydracids generally, and their salts, apply to cyanogen, hydro-cyanic acid, and their combinations. But this is not all. The cyanurets of iron,

and especially the proto-cyanuret just described, are commonly regarded as analogous in function with cyanogen itself; that is to say, compounds performing the functions of a simple body. Hence, has arisen the term "ferro-cyanogen,"—a body which, by combining with hydrogen generates hydro-ferro-cyanic acid, whose functions are like those of any other hydracid. Perhaps the bearing of these remarks will be more obvious if we take a special case for exemplification. That case may be the salt known as *prussiate of potash.*

Its composition is as follows:—

1 equivalent Iron 2 equivalents Potassium 2 equivalents Cyanogen	1 equivalent Anhydrous Prussiate of Potash.

Adopting the theory of its being a mere binary compound of cyanide of iron with cyanide of potassium, its composition will stand thus—

1 eq. Iron 1 eq. Cyanogen	1 eq. Cyanide of Iron	1 eq. Anhydrous Prussiate of Potash
2 eq. Potassium 2 eq. Cyanogen	2 eq. Cyanide of Potassium	

and will be represented by the symbol FCfy + 2 KCy.

But if we assume the existence of the compound radical *ferrocyanogen*, then anhydrous prussiate of potash must be regarded as anhydrous ferocyanide of potassium, and its constituents will be grouped as follows:—

1 eq. Iron 3 eq. Cyanogen	1 eq. Ferrocyanogen	1 eq. Ferrocyanide of Potassium
2 eq. Potassium		

Hydrogen, it will be remembered, possesses many of the relations of a metal, with which it frequently changes places, atom for atom. This fact being remembered, it will not seem extraordinary that the two equivalents of potassium in the preceding compound should be capable of substitution by hydrogen, as in the following scheme:—

1 eq. Iron 3 eq. Cyanogen	1 eq. Ferrocyanogen	1 eq. Ferrocyanide of Hydrogen
2 eq. Hydrogen		

Now, as the chloride of hydrogen is termed hydrochloric acid, the bromide of hydrogen hydrobromic acid, &c., by a parity of usage the ferrocyanide of iron should be denominated *hydroferrocyanic acid.* Ferrocyanide of hydrogen and *hydroferrocyanic acid* are, therefore, synonymous terms, both indicating the compound in which two equivalents of hydrogen have taken the place of two equivalents of some other simple body. The radical of hydroferrocyanic acid, instead of being represented symbolically by the initials of its constituents, is indicated by the symbol Cfy; therefore hydroferrocyanic acid will be symbolically designated thus, Cfy2H.

Properly speaking, the philosophy of cyanogen belongs to the department of organic chemistry, where it will be treated more in detail. I have only entered upon its description here to the extent necessary for explaining the nature of its combinations with iron.

Double Cyanide of Iron and Potassium.—Ferrocyanide of Potassium.—This salt is of great importance, both in the laboratory and the arts. It is formed commercially in large quantities, and moderately pure.

Preparation.—(1). The oldest and most usual method of generating ferrocyanide of potassium (prussiate of potash) is as follows:—Fragments of animal matters, such as horns, hair, hoofs, &c., are first calcined in close vessels, so that highly nitrogenized animal charcoal may result. The latter is now mixed with carbonate of potash, and heated in an iron vessel by a reverberatory flame. The materials fuse into a mass, which is stirred from time to time with an iron rod. Cyanuret of iron and cyanuret of potassium are formed; by combination they generate ferrocyanide of potassium, which being washed out by water, and the solution evaporated, yields the well-known crystals of prussiate of potash. They are composed of one equivalent of ferrocyanide of potassium, combined with three equivalents of water, and consequently are represented by the formula—

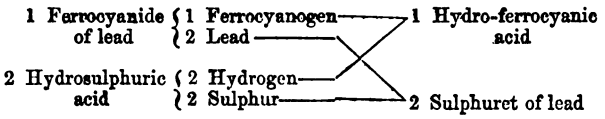
$$FeCy + 2KCy + 3HO.$$

(2). By the direct union of carbon and nitrogen in contact with carbonate of potash. This process is now conducted on the large scale, and is of peculiar interest. The stages of the operation are as follow:—Wood charcoal, having been strongly impregnated with solution of carbonate of potash, is heated in brickwork, and exposed to the agency of a mixture of carbonic acid and nitrogen gases, formed by transmitting atmospheric air through burning coke. This operation having been continued for about ten hours, the charcoal is allowed to cool, removed, and lixiviated with water. The fluid of lixiviation is next boiled in an iron vessel, with finely-powdered native peroxide of iron (spathic iron), when a solution of prussiate of potash is obtained, from which the salt separates by evaporation.

Crystallized ferrocyanide of potassium easily loses its three equivalents of water by a gentle heat. If the temperature be raised still higher, the salt decomposes, with the evolution of hydrogen. On lixiviating the fixed residue, cyanide of potassium is washed out, and a black carburet of iron remains, having the composition of Fe_2C_2.

Solution of prussiate of potash is a valuable test, indicating the presence of numerous metals by distinctive tints. Thus, with the kaligenous and terrigenous metals generally, it yields no colouration or precipitate; but with solutions of nearly all the calcigenous metals, in almost every state of combination, it furnishes either a distinctive tint, or a precipitate, or both. With solutions of copper, titanium, molybdenum, and uranium, the colour furnished is brown; with solutions of absolutely *pure* protosalts of iron, white; but with solutions containing even the slightest amount of a persalt of iron, blue. Practically, therefore, it yields a blue colour with *all* the solutions of iron which occur in the ordinary course of analysis. With the generality of calcigenous metals remaining, prussiate of potash yields a white precipitate. In the greater number of these bodies, the potassium of the ferrocyanide of potassium is displaced by the new metal. For example, ferrocyanide of copper is represented by the formula 2Cu + Cfy; the ferrocyanide of lead by 2Pb + Cfy.

By acting on the ferrocyanide of lead by hydrosulphuric acid, decomposition ensues; sulphuret of lead is thrown down, and hydro-ferrocyanic acid is evolved. Hydroferrocyanic acid yields precipitates with metallic solutions precisely identical with those yielded by ferrocyanide of potassium. The decomposition which takes place is illustrated by the appended diagram—



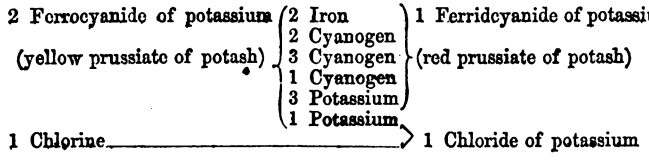
Thus obtained, it is dissolved in water; by evaporating the solution in vacuo over strong sulphuric acid, it may be procured in crystals. There is another method of preparing hydro-ferrocyanic acid; by adding hydrochloric acid to a concentrated aqueous solution of prussiate of potash free from air, and agitating the mixture with ether; by which treatment crystals of the acid are thrown down.

Ferrosesquicyanide of Potassium, or Ferridcyanide of Potassium (Red Prussiate of Potash).

This is another important salt, containing iron in its acid or electro-negative component.

Preparation.—By transmitting chlorine through a solution of yellow or common prussiate of potash, until the solution ceases to furnish a blue precipitate with persalts of iron, and evaporating. During the operation of transmitting chlorine, the liquor must be continually agitated, and the chlorine must not be supplied in excess.

The decomposition which ensues may be thus represented by a diagram:



or thus, in chemical symbolic notation,

$$2(FeCy + 2KCy) + Cl = (3KCy + Fe_2Cy_3) + KCl.$$

Properties.—This salt is less soluble than yellow prussiate of potash, only one part being dissolved in about forty of cold water. Like the preceding, it is a valuable test for several calcigenous metals, more especially iron. With proto-compounds of iron it yields a white, with per-compounds a blue precipitate, whereas yellow prussiate of potash acts in the reverse order, yielding a white precipitate with proto-compounds of iron, and a blue precipitate with per-compounds of the same metal. Similarly to yellow prussiate of potash, the compound under consideration yields a precipitate with solutions of lead, and this precipitate being decomposed by dilute sulphuric acid, yields a distinct and somewhat permanent hydracid, *ferrosesquicyanic acid*, or *ferridcyanic acid.*

Ferridcyanide of lead is composed, as indicated, by the formula $3PbCy + Fe_2Cy3$, and the composition of hydro-ferridcyanic acid is represented by the formula $3HCy + Fe_2Cy_3$. By carefully evaporating a solution of hydroferridcyanic acid it is obtained in the state of crystals.

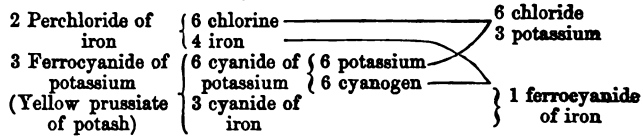
Prussian Blue.

Under the generic name of Prussian blue are comprehended several important cyanogen compounds of iron, of which I shall only specially advert to two: common prussian blue, which is the result obtained by adding yellow prussiate of potash to a

persolution of iron, and Turnbull's Prussian blue generated by adding red prussiate of potash to a protosalt of iron.

Common Prussian Blue.

Preparation.—This compound is generated, as already indicated, when solution of yellow prussiate of potash is added to a solution of a persalt of iron. The decomposition which ensues is represented by the subjoined diagram, in solutions where perchloride of iron is supposed to have been employed.



or, in chemical symbolic notation, as follows,

$$2Fe_2Cl_3 + 3(FeCy + 2KCy) = 6KCl + (3FeCy + 2Fe_2Cy_3).$$

whence it appears that the formula of common prussian blue (ferro-cyanide of iron) is

$$3FeCy + 2Fe_2Cy_3 \text{ or, } 3Cfy + 4Fe.$$

Properties.—Somewhat resembling indigo in general appearance, but far less permanent when subjected to chemical re-agents. In water and weak acids it is insoluble. Strong sulphuric acid decomposes it, with the production of a white compound. Alkalies also destroy its colour instantaneously. Heated in the open air it burns, leaving a residue of peroxide of iron; and exposed to destructive distillation it is decomposed into cyanide of ammonium, water, carbonate of ammonia, and carburet of iron.

Turnbull's Prussian Blue.

The method of preparing this compound has already been indicated. It possesses a brighter tint than the preceding compound, and is employed for similar purposes.

CHROME, OR CHROMIUM.

Atomic or equivalent weight	26·7
Specific gravity (about)	5·9

General Remarks.—This important metal derives its name from χρῶμα, colour, on account of the varied tints afforded by its combinations. *Chromium* was demonstrated to be a metal by Vauquelin, in 1787; he succeeded in obtaining it from oxide of chromium, but not in a pure condition.

Preparation.—The process followed for obtaining chromium is the counterpart of that adopted for the preparation of manganese; sesquioxide of chrome being intimately mixed with charcoal-powder, sugar, and oil, charcoal, sugar, and coal-tar, or some materials equally rich in carbon, is raised into an earthenware crucible, lined with charcoal, and exposed to the highest heat of a smith's forge. A mass remains, metallic in appearance, and which was once considered to be pure chromium; it, however, bears the same relation to chromium that cast iron bears to the pure metal,—*it is carburetted.* To obtain it pure the preceding result is to be powdered, then intimately mixed with green oxide of chromium, and exposed a second time to the highest heat of a smith's forge, in a crucible of porcelain lined with charcoal, and contained in one of Hessian, or Cornish ware.

By this operation oxygen from the oxide of chromium unites with the carbon of the carbonaceous mass, which escapes in the condition of carbonic oxide and carbonic acid, pure chromium remaining in the state of button or ingot, if the heat have been sufficient.

Properties.—Chromium has a full white metallic lustre; it is very brittle, and sufficiently hard to scratch glass. Dry atmospheric air, at ordinary temperatures, does not oxidise it perceptibly; but it is readily oxidised by heating it to redness. Hydrochloric acid and dilute sulphuric acid readily dissolve it.

Chromium with Oxygen.—The oxygen compounds of chromium are numerous. Taken as a class, they present analogies to the oxygen compounds of iron; but one is analogous in composition to permanganic acid. The following is a tabular arrangement of the oxygen compounds of chromium:—

	Chromium.	Oxygen.
1. Protoxide of chromium	1	1 (?)
2. Sesquioxide of chromium	2	3
3. Compound of the two preceding in single atomic proportions	3	4
4. Chromic acid	1	3
5. Combination of chromic acid and protoxide of chrome	2	4
6. Perchromic acid	2	7

Protoxide of Chromium.

Preparation and Properties.—Solution of potash being added to solution of protochloride of chromium, protoxide of chromium is thrown down in the state of a brown hydrate. The precipitate is, however, not permanent. Having a great affinity for oxygen, it decomposes water almost as soon as formed; and if the solution be hot, the decomposition proceeds with remarkable activity. The result of this decomposition is the production of the hydrate of the oxide Cr_3O_4, or rather, perhaps, $CrO_1\ Cr_2O_3$, seeing that it is regarded as analogous with the magnetic oxide of iron. By heating this latter hydrated oxide in a glass tube, further decomposition takes place; the equivalent of oxygen possessed by the water of hydration is retained and hydrogen evolved. The composition of protoxide of chrome is *assumed* to be as represented in the tabular view just given. The determination of its composition by analysis has not been accomplished.

Salts of Protoxide of Chromium.—On account of the avidity of this oxide for oxygen, but little of the salts in question is known. The acetate and the double sulphate of protoxide of chromium and potash are the only proto-oxygen salts of chrome which have been distinctly formed. Many of the qualities, however, of the protoxide of chromium are manifested by the proto-chloride of the metal. The following are amongst the most remarkable:—

Caustic potash throws down at first a brown precipitate of hydrated oxide, almost immediately changing into the brown hydrated magnetic oxide; hydrogen being simultaneously evolved. Hydrosulphates yield a black precipitate, but hydrosulphuric acid none. Corrosive sublimate, when added to it, throws down calomel; and chlorine, nitric acid, and many other oxidising agents convert the protoxide into the green, or sesquioxide.

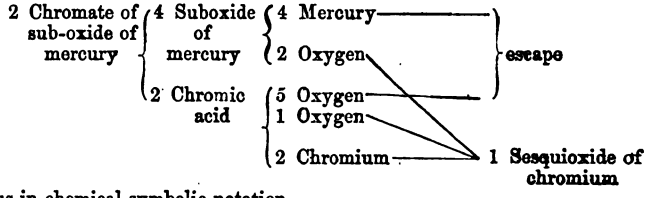
Sesquioxide of Chromium.

General remarks.—In its general characteristics this oxide is analogous to the

sesquioxide of iron, acting the part of a feeble base, and yielding in many cases salts of two colours (green and violet) with the same acid.

Preparation.—This oxide, in a hydrated condition, may be thrown down from any sesquisalt of chromium by the addition of ammonia; in the anhydrous condition it can be obtained by many processes, amongst which the following may be enumerated:—

(1) By decomposing by heat, the chromate of the sub-oxide of mercury, when oxygen and metallic mercury are evolved, and green sesquioxide of chromium remains. The decomposition which ensues is determined by the tendency of oxygen and mercury to be volatilized by heat. It is represented by the following diagram:—

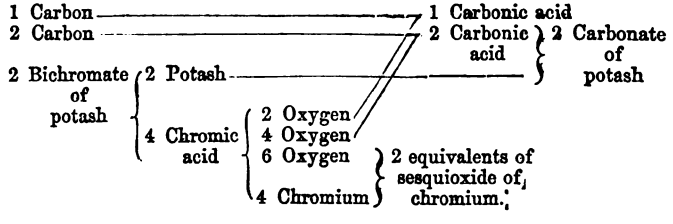


Or thus in chemical symbolic notation—

$$2(Hg_2O, CrO_3) = Cr_2O_3 + 4Hg + 5O.$$

Remark.—The chromate of sub-oxide of mercury here referred to is prepared by mixing together solutions sub-nitrate of mercury and of chromate of potash. The red precipitate which falls is the substance under consideration.

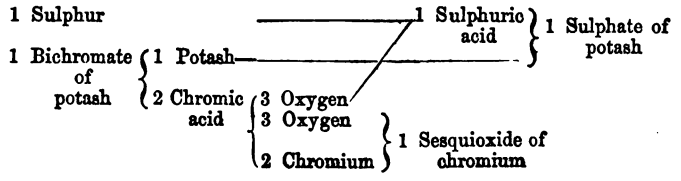
(2) By the calcination of bichromate of potash with charcoal, sugar, starch, or *generally* any organic body rich in carbon; and lixiviating the product with water. The decomposition which ensues is represented as follows by a diagram, and by chemical symbolic notation:—



$$2(KO, 2CrO_3) + 3C = 2(KO, CO_2) + CO_2 + 2Cr_2O_3$$

(3) By calcining one part of bichromate of potash and about two parts sulphur, a mixture of sulphate of potash and sesquioxide of chromium is obtained. On treating this with water, the alkaline salt dissolves out, and the chrome-oxide is isolated. It will be seen that in this operation the sulphur acts the part of carbon in the preceding decomposition; both have a strong affinity for oxygen, and remove that element from the chromic acid contained in the bichromate; carbon yielding a carbonate under these circumstances, sulphur a sulphate. Oxide of chromium prepared by this process is frequently contaminated by a little sulphur, which, however, may be burned away in the condition of sulphurous acid, and the oxide left pure.

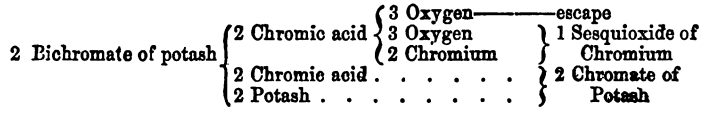
The decomposition which results from the preceding operation is thus represented:—



$$KO,2CrO_3 + S = Cr_2O_3 + KO,SO_3$$

Remark.—An excess of sulphur over and above the theoretical atomic proportion is requisite in conducting this operation, in as much as a portion becomes volatilized, thus taking no part in the subsequent action.

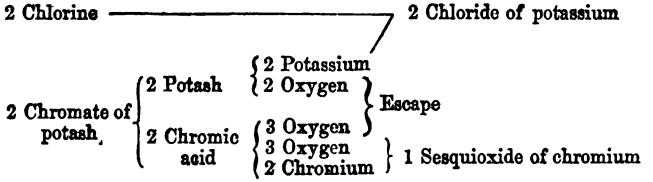
(4) By heating bichromate of potash to whiteness the salt is decomposed, oxygen being evolved, and neutral chromate of potash mixed with sesquioxide of chromium remaining. The neutral chromate of potash being soluble in water, and the sesquioxide of chromium insoluble in that medium, separation of the two can be readily effected. The decomposition is thus represented:—



Or,

$$2(KO,2CrO_3) = Cr_2O_3 + 3O + 2(KO,CrO_3).$$

(5) By heating chromate of potash to redness in a tube of porcelain, and transmitting over it a current of chlorine. Chlorine by abstracting and combining with potassium forms chloride of potassium; and chromic acid being unable, under the conditions of the experiment, to exist alone, is decomposed into oxygen and sesquioxide of chromium.



Or,

$$2(KO,CrO_3) + 2Cl = 2KCl + Cr_2O_3 + 3O.$$

(6) By transmitting the vapour of chloro-*chromic acid* (a preparation to be hereafter described) through a red-hot porcelain tube. The sesquioxide prepared by this method is obtained in crystals of extreme beauty. Their colour is very dark green, almost black, and of sufficient hardness to scratch glass. In form they are octahedral —isomorphous with native silicate of alumina, or corundum. The decomposition

which ensues when chlorochromic acid is transmitted through the red-hot tube is as follows :—

2 Chlorochromic acid	2 Chlorine	Escape
	1 Oxygen	
	3 Oxygen	1 Sesquioxide of chromium
	2 Chromium	

Or,

$$2CrO_2Cl = Cr_2O_3 + 2Cl + O.$$

Salts of Sesquioxide of Chromium.—We have seen that the sesquioxide of chromium is green, a colour which it imparts to flame; and here arises an important qualitative distinction, one especially useful a blowpipe indication of the metal, and of frequent application to the arts of porcelain and glass-painting. A combination of sesquioxide of chrome, lime, and stannic acid is also employed as beautiful red pigment. Although acids combine with this oxide, they do this readily only under particular circumstances, namely, whilst it is hydrated, or before it has been strongly heated; after this only strong acids combine with it, and with considerable difficulty.

Upon the whole it is rather an acid, than a basic substance; it combines with several bases, of these the protoxide of iron furnishes the most remarkable example constituting the mineral known by the name of *chromate of iron*, or more properly *chrome iron*. The constitution of this body is $FeO\ Cr_2\ O_3$. It sometimes occurs crystallized in regular octahedrons, being, therefore, the analogue of magnetic oxide of iron, and the spinelle ruby. More frequently, however, it occurs in the amorphous state. Its principal localities are Lancashire and Cheshire counties, Pennsylvania, Sweden, and the Uralian mountains.

Salts of sesquioxide of chrome may be recognized by the following general characteristics. With many acids it forms, as I have remarked, two series of salts, the green and the violet-coloured. There are, for example, a green and a violet sulphate, each of which yields a precipitate of distinct hue when ammonia is added; that of the green sulphate being bluish, the other greenish. Solutions of potash and of soda produce an almost similar effect. Alkaline carbonates yield with both varieties a greenish precipitate. Hydrosulphates yield a black precipitate; but hydrosulphuric acid none. Fused with borax the sesquioxide of chromium, like the protoxide of that metal, yields a blue glass; and fused with alkaline carbonates or nitrates, alkaline chromates are developed, known by the yellow colour of their solutions.

Chrome Alums.—Sesquioxide of chromium, having the same atomic constitution with sesquioxide of iron, and sesquioxide of alumina, and being moreover isomorphous with these, may take their place in chemical combinations. Hence, we have the interesting bodies *chrome alums*. Three of these are known, as follows :—

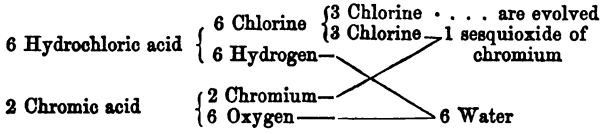
Potash—Chrome alum	$Cr_2O_3 3SO_3 + KO,SO_3 + 24HO$
Soda—Chrome alum	$Cr_2O_3 3SO_3 + NaO,SO_3 + 24HO$
Ammonia—Chrome alum . . .	$Cr_2O_3, 3SO_3 + (NH_3,HO)SO_3 + 24HO$

Chromic Acid.

Preparation.—There are several methods of preparing chromic acid; but the most simple is the following :—Four parts of bichromate of potash powdered are gradually mixed with three of concentrated sulphuric acid at a temperature of from 130° Fah. to

140 Fah. The result of this operation is bisulphate of potash which remains in solution, and crystals of chromic acid which deposit on cooling. The crystals are to be drained from much of their adherent sulphuric acid by being placed in a funnel supplied with a loosely fitting plug of asbestos, and finally drained dry by spreading them on porous porcelain. Still they retain a little sulphuric acid: they should, therefore, be re-dissolved in a small quantity of water, solution of chromate of baryta added, until a precipitate no longer takes place, and recrystallized by evaporation in vacuo.

Properties.—Crystals of chromic acid have a beautiful red colour when cold, but when heated this colour deepens almost to blackness. If the heat be increased short of redness, the chromic acid decomposes into sesquioxide of chromium, and oxygen. Chromic acid, on account of the amount of oxygen which it contains, and the facility with which the latter is evolved, is a powerful oxidising agent. Thus, when mixed with alcohol, sugar, or one of many other carbonaceous substances, it suffers decomposition, and sesquioxide of chromium is generated; the change being indicated by the occurrence of a green colour. Treated with hydrochloric acid, sesquichloride of chrome results, and chlorine is evolved, in accordance with the following diagram and formulæ.



$$2\,CrO_2 + 6\,HCl = Cr_2Cl_3 + 6HO + 3Cl.$$

Chromic acid unites with sesquioxide of chromium in several proportions; but the resulting compounds have not been much studied.

Chromic Acid with Bases (Chromates).

Chromic acid we have seen to be *isomeric* with sulphuric acid; in other words, it has a similar atomic constitution. It readily combines with most bases, yielding compounds *isomorphous*, or belonging to the same crystalline system, with the sulphates. All the metallic chromates, with the exception of those of *lime*, *strontia*, *magnesia*, are insoluble, or nearly so. Chromic acid furnishes two well characterized series of salts, neutral chromates and bichromates; the former yellow, the latter orange. Both yield a yellow precipitate with salts of lead and bismuth; red with those of mercury; and very deep red with those of silver. Similarly to uncombined chromic acid, the chromates are decomposed into sesquioxide of chromium, and a chloride of the radical of the base—when heated with hydrochloric acid.

Perchromic Acid.

Preparation.—By adding peroxide of hydrogen to chromic acid the latter is raised to a higher state of oxygenation, and becomes perchromic acid, which may be dissolved in ether, but which has never been isolated nor obtained in combination with bases.

Properties.—Solutions containing perchromic acid possess a beautiful blue tint.

Chromium with Chlorine (Chlorides of Chromium).

Of these compounds two are known, the *protochloride* and the *sesquichloride*; corresponding with the protoxide and the sesquioxide respectively.

Sesquichloride of Chromium.

Preparation.—Precisely like chloride of aluminium, already described (page 427). It condenses in the form of crystals, having a light pink colour, in the cool portion of the tube.

Properties.—Quite insoluble in cold water, but boiling water takes up a little generating a green-coloured solution. In water, however, holding a faint trace of the compound, next to be described—protochloride of chromium—in solution, the sesquichloride readily dissolves, with the evolution of much heat.

Protochloride of Chromium.

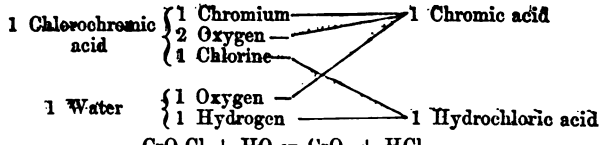
Preparation.—By transmitting hydrogen gas over anhydrous sesquichloride, heated to redness in a porcelain tube.

Properties.—A white compound, soluble in water, the solution being blue, rapidly absorbing oxygen from the air, and becoming converted into oxychloride. Like solutions of protochloride, and of sesquichloride of iron, solutions of protochloride of chromium have the property of absorbing binoxide of nitrogen.

Chlorine with Chromium and Oxygen—Chlorochromic Acid.

Preparation.—Fuse in an earthen crucible a mixture of 10 parts by weight of chloride of sodium with 17 parts of bichromate of potash, pour the fused mass on a flat stone or metallic sheet; break it when cold, and distil it in a retort with 30 parts by weight of strong sulphuric acid. Chlorochromic acid is evolved, and may be condensed in a receiver kept cold with ice.

Properties.—A deep red fluid, so much like bromine in appearance, that it is not easy to distinguish one from the other. Specific gravity 1·71; boiling point, 248° Fah. It is decomposed, by contact with water, into chromic and hydrochloric acid, according to the following scheme.



$$CrO_2Cl + HO = CrO_3 + HCl.$$

Compounds of Chromium with Sulphur and Nitrogen.

A sulphuret or sulphide of chromium may be produced by transmitting the vapour of bisulphide of carbon over sesquioxide of chrome heated to redness in a tube of porcelain. The substance has a crystalline aspect, somewhat resembling native graphite in appearance. Its composition is represented by the formula $Cr_2 S_3$. A compound of chromium with nitrogen may be formed by heating sesquichloride of chromium in ammoniacal gas. It occurs as a brown powder, the atomic composition of which has not been determined.

NICKEL.

Atomic or equivalent weight	= 29·6
Specific gravity	= 8·8

History and Natural History.—Nickel was recognized as a distinct metal by

Cronstadt and Bergmann in 1751. It is obtained from an ore termed by the Germans *Kupfer nickel*, or false copper, because it somewhat resembles a copper ore in general appearance, but contains none. When the ore in question was found to contain a new metal, the term *nickel* was retained. Nickel is also obtained from a commercial article termed speiss, being the residue of the ore from which cobalt is extracted. Both *Kupfer nickel* and *Speiss* are arseniurets of the metal.

Nickel is isolated from the arsenic with which it is associated in the preceding compounds by the following treatment. The ore is first dissolved in a mixture of dilute nitric and sulphuric acids. The nitric acid converts the arsenic into arsenious acid, and nickel being changed into oxide of nickel, unites with sulphuric acid and forms sulphate of oxide of nickel. The liquor is now evaporated, when most of the arsenious acid crystallizes and is deposited. Carbonate of potash is now added, and the solution being crystallized yields a double sulphate of nickel and potash. This salt may at first be slightly contaminated with arsenic, iron, and copper; by solution and crystallization twice, or three times, it may be completely freed from the former metal. Copper may be separated by precipitation with hydrosulphuric acid (which neither throws down iron or nickel), and finally, nickel oxide may be obtained free from oxide of iron by the action of liquor ammoniæ, which dissolves the former, but leaves the latter intact. Oxalic acid precipitates the oxide of nickel from its ammoniacal solution in the condition of oxalate of nickel; which being heated leaves metallic nickel.

Preparation.—One method of obtaining nickel in the metallic state has just been described, *viz.*, by decomposing the oxalate of nickel by heat. A degree of heat short of redness suffices to effect this decomposition, but the resulting nickel only aggregates into a metallic button when the heat applied is intense. If the metal be required in this condition, portions of dried oxalate are to be rammed into a charcoal-lined earthen crucible, and exposed for not less than two hours to the strongest blast of a smith's forge. Metallic nickel may also be obtained in a spongy state by transmitting a current of hydrogen gas over oxide of nickel heated to redness in a porcelain tube; or in the condition of metallic button by exposing the oxide, mixed with sugar, starch, charcoal powder, or other carbonaceous materials to the highest heat of a smith's forge in a charcoal-lined crucible. Nickel produced by the operation last mentioned is *carburetted*, or, in other words, holds in combination a small portion of carbon; it therefore has the same relation to pure nickel, that cast iron and steel have to pure iron.

Properties.—Nickel is a white metal, inclining to gray, very magnetic at ordinary temperatures, but loses that property when heated to 400° Fah. Its surface bears a high polish, and does not tarnish much by exposure to ordinary atmospheric agencies at common temperatures; when heated, however, its surface becomes covered with an oxide. Its proper chemical solvents are hydrochloric and sulphuric acids. Nickel, when obtained as a metallic button, has the aspect of a brittle metal; it is, however, malleable to some extent, and may be drawn out into wire.

Compounds of nickel with oxygen.—Oxides of *Nickel.*—Of these compounds two are known: the protoxide and sesquioxide of nickel

Protoxide of Nickel.

Preparation and properties.—When a solution of potash, or of soda, is added to any protosalt of nickel, the protoxide of that metal in the hydrated state is thrown down. The latter being exposed to heat in a close vessel, yields anhydrous protoxide of nickel. It may also be obtained by calcining the hydrated carbonate of nickel, in place of the

hydrated oxide of that metal;—or finally, by decomposition of the nitrate at a very high temperature. Hydrated protoxide of nickel has a beautiful green colour; anhydrous oxide of nickel is gray or brown.

Sesquioxide of Nickel.

Preparation and properties.—This oxide may be generated by suspending the protoxide in water, and either transmitting through it a current of chlorine, or boiling it with a solution of commercial chloride of lime. It is a black powder, which evolves oxygen when heated, and leaves protoxide. It does not form any well-defined and permanent salts.

Characteristic qualities of nickel solutions, especially solutions of the protoxide.—The solutions of nickel which usually occur in the course of mineral analysis, are of the protoxide or the protochloride, which latter belongs to the same practical category with the former. All these solutions, and the salts crystallized out of them, are characterized by a green tint; in this respect presenting some analogy to the salts of copper, and certain protosalts of iron; the green tint, however, of nickel salts is far more decided than of the former. Nickel solutions yield no precipitate with hydrosulphuric acid; in which respect they resemble, amongst calcigenous metals, the solutions of iron, cobalt, manganese and uranium. With hydrosulphate of ammonia, and the hydrosulphates generally, a black precipitate is furnished. Ferrocyanide of potassium generates a whitish precipitate, and solution of ammonia a green precipitate, re-dissolved by adding excess of ammonia, and then generating a deep blue liquid; by the last two characteristics nickel solutions will be seen hereafter to assimilate themselves to those of copper. Carbonates of alkalies, also alkaline arseniates and phosphates, throw down a pale green precipitate.

Oxygen Salts of Nickel.—Of these, the sulphate of the protoxide of nickel is the best defined and the most beautiful; it may be readily prepared by saturating dilute sulphuric acid with protoxide of nickel and evaporating the solution. If the solution be only evaporated until a pellicle forms on its surface, and set aside to crystallize, the resulting crystals hold seven equivalents of water of crystallization; but if the evaporative process be continuous, the resulting crystals only contain six equivalents of water of crystallization. In both conditions of hydration the crystals of sulphate of nickel are very beautiful. Their colour is an intense grass-green.

Alloys of Nickel.—The most important of these alloys is German silver, a material now in extensive use as a substitute for silver itself. German silver is composed of 100 parts copper, 60 of zinc, and 10 of nickel. The chief employment of German silver at this time is as a body on which pure silver or gold may be deposited by the operation of electrotyping. For this purpose it answers well; but the most casual observation suffices to distinguish the metal from silver, when not thus disguised.

COBALT.

Equivalent or atomic weight . . .	29·5
Specific gravity	8·5

History and Natural History.—Cobalt was first recognized as a distinct metal by Brandt in 1733. It occurs associated with nickel, from which it can only be separated completely by tedious analytical processes.

Preparation.—The processes had recourse to for obtaining nickel in the pure

metallic state, so exactly resemble those already described for obtaining cobalt, that any further description of them is unnecessary.

Properties.—Cobalt, when obtained from its oxide decomposed by a current of hydrogen gas, at a low furnace temperature, is a gray powder, which takes fire on coming into contact with the atmosphere, and is converted into oxide; by effecting the same decomposition at a high temperature the resulting cobalt is still pulverulent, but no longer pyrophoric. When obtained by the decomposition of the oxalate of cobalt, in contact with carbonaceous matter, and at a high temperature, the resulting cobalt occurs in the form of a metallic button, having the lustre of steel, bearing a polish, very brittle, having the magnetic property in a very high degree, and less oxidisable than iron when exposed to the influence of a moist atmosphere. The proper solvents for cobalt are the sulphuric and the hydrochloric acids, with either of which it yields a solution, hydrogen gas being evolved.

Cobalt with Oxygen.

Oxides of Cobalt.—There are two known oxides of cobalt, both capable of yielding salts by union with acids; they are the protoxide, CoO, and the sesquioxide, Co_2O_3.

Protoxide of Cobalt.

General Remarks.—All ordinary salts of cobalt contain either the oxide or its corresponding haloid radical, the salts of which may, for the most part, be recognized by their red or roseate colour; some are red only when diluted to a certain point. This remark applies for instance to the protochloride of cobalt, the solution of which assumes, on being concentrated, a beautiful azure tint, but is red when diluted. The difference of tint in this example may be the result of difference between hydration and dehydration; it may, with equal probability, be referable to allotropism, an assumption which is rendered probable by the demeanour of crystallized chloride of cobalt at various degrees of temperature. Whilst cold this substance is red, but when heated it becomes blue; no loss of water, however, takes place, nor is any other change of chemical composition recognizable. This mutation of colour effected by the chloride of cobalt, has suggested its employment as a sympathetic ink. If letters be traced with a weak solution of chloride of cobalt, they are at first invisible, because the rose-coloured modification of the salt is not sufficiently pronounced to be apparent; by heating the paper, however, the cobalt solution becomes concentrated, when assuming its blue tinge the letters written with it are easily seen. By allowing the paper to cool, the blue colour vanishes, and by heating it reappears; changes which may be determined indefinitely, provided the degree of heat employed be not too considerable.

Preparation.—The protoxide of cobalt in combination with water, or "*hydrated,*" may be obtained by treating any protosalt of cobalt with a solution of potash or soda, or of ammonia, provided the cobalt salt do not contain excess of acid. The hydrated protoxide thus produced is a light blue precipitate. When heated strongly the water of hydration is evolved, and the gray anhydrous protoxide remains.

Salts of Protoxide of Cobalt.—All the protosalts of cobalt admit of preparation by the direct neutralization of it with acids, and evaporation of the residue. Many can also be prepared, by processes not so direct, from ores of cobalt, especially the native arseniuret of cobalt, termed cobalt glance. When a pure salt of cobalt is desired from cobalt glance, the latter should be chosen free from nickel, with which it is frequently

associated. The cobalt ore from Tunaberg, in Sweden, being purest, is best adapted to the purpose: it may be treated by either of the two following processes:—

Process 1.—The pulverized ore is spread on a muffle, and heated until all its sulphur has been converted into sulphurous acid and evolved, and a considerable portion of its arsenic has been also evolved in the form of arsenious acid. Simultaneously with the evolution of one part of the arsenic as arsenious acid, another part unites with oxygen, and becomes converted into arsenic acid; which latter no sooner forms than it combines with the cobalt (which has by this time become oxidised), forming arseniate of cobalt. At length the evolution of arsenious acid ceases, when the operation is advanced another stage; the material is mixed with charcoal powder, and the current of atmospheric air intercepted by closing up the muffle. The charcoal, by virtue of its deoxidising property, converts the arseniate into the arseniuret, which, on throwing open the muffle, is converted into arsenious acid, which in its turn escapes. Theoretically, the *whole* of the arsenic should be capable of separation by the methods indicated; but practically this is not the case. The last traces of arsenic are usually removed by roasting the cobaltic product with carbonate of soda and nitre, by which treatment the arsenic forms arsenic acid, which in its turn immediately unites with the soda, forming carbonate of soda. Inasmuch as arseniate of soda is soluble in water, whereas oxide of cobalt is not, the means of effecting their separation is obvious. Nevertheless, oxide of cobalt thus produced is rarely or ever pure, usually being mixed with oxide of iron. It should, therefore, be dissolved in nitric acid, the excess of acid driven off by evaporation, the pernitrate of iron redissolved in water, and the peroxide of iron thrown down by carbonate of soda; after which the oxide of cobalt may be thrown down as oxalate by the addition of oxalic acid, or as protoxide by treatment with solution of potash or of soda.

Process 2.—Instead of the operation just described, the powdered cobalt glance may be incorporated with sulphur and carbonate of soda, and the mixture ignited in a crucible, by which treatment a button, composed of a mixture of sulphuret of cobalt, arseniuret of cobalt, and sulphuret and arseniuret of sodium results. This button, being comminuted and digested with weak oil of vitriol, hydrosulphuric acid is evolved, and solution of sulphate of cobalt remains, which deposits crystals of that salt on evaporation.

Sulphate of Cobalt.—This beautiful salt may either be obtained indirectly by the process last described, or directly by saturating sulphuric acid with oxide of cobalt, and subsequently evaporating. The salt may be obtained either holding seven or six equivalents of water of crystallization, dependent on the temperature employed in the evaporative operation.

Nitrate of Cobalt may easily be formed by the direct process. When heated, protoxide of cobalt, generally mixed with a variable portion of peroxide, remains.

Oxalate of Cobalt is an interesting salt, on account of its tendency to insolubility in various solutions; thus furnishing a means of throwing down oxide of cobalt from certain mixed solutions. Oxalate of cobalt occurs in the form of rose-tinted crystals when solution of oxalic acid is added to solution of sulphate, nitrate, or chloride of cobalt.

Combinations of Cobalt with Silicic Acid and Silicates.—Silicic acid unites by fusion with oxide of cobalt, and forms silicates of that base. The silicates of cobalt, however, are of much less interest and importance than the double silicate of cobalt and potash, to which the term *smalt* is applied. Smalt has a light blue colour, and is extensively prepared in Saxony and elsewhere as a pigment by heating the roasted

native arsenio-sulphuret of cobalt with siliceous sand, and carbonate of potash in large crucibles. The blue mass resulting from this operation is broken, then finely powdered, and lastly separated from all coarser particles by suspension in water. Zaffre is a kind of superior smalt.

Cobalt-Ultramarine, or Thenard's Blue, is made by mixing hydrate of alumina with phosphate of cobalt, and heating the mixture to redness in crucibles holding a little peroxide of mercury, which latter, by evolving oxygen, improves the colour of the resulting compound.

General Characteristics of Cobalt in Solution (Protosalts).—(1) The most striking test of cobalt in any state is the magnificent blue tint it imparts to glass. Salt and zaffre, in point of fact, are merely glasses coloured blue with cobalt. For the purpose of developing this colour as a qualitative test of the existence of cobalt, borax is usually the material chosen for colouration. A platinum wire being bent into a small loop is moistened, dipped in powdered borax, and heated to redness in the blow-pipe flame, when a colourless bead results. The bead is now moistened, dipped into a solution of cobalt, or a powder containing that metal, and again heated to redness, when the beautiful blue tint, so indicative of the presence of cobalt, is immediately apparent.

(2) Potash solution throws down the blue hydrated protoxide of cobalt, the tint of which alters to red on the application of heat.

(3) Ammonia throws down a blue precipitate soluble in excess of ammonia, the solution being brown.

(4) Solution of carbonate of potash of soda, or of ammonia, throws down the pinkish carbonate of cobalt. If carbonate of ammonia be employed, the precipitate thrown down is soluble in excess of the reagent.

(5) Hydrosulphuric acid yields no precipitate, or alteration of colour, with solutions of cobalt; but hydrosulphate of ammonia (sulphide of ammonium) yields a black precipitate.

(6) Ferrocyanide of potassium throws down the ferrocyanide of cobalt, having a dull green colour.

Sesquioxide of Cobalt.

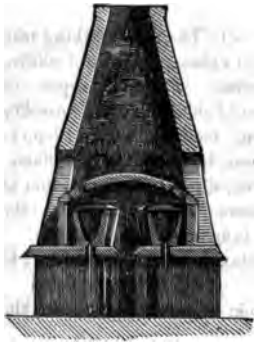
Preparation.—Hydrated protoxide of cobalt is suspended in water, and a current of chlorine transmitted. By this treatment one portion of the oxide is decomposed, its metal uniting with chlorine to form a chloride, and its oxygen uniting with another portion of protoxide to form sesquioxide of cobalt, which is thrown down. If, now, to the liquor holding protochloride of cobalt in solution potash be added, the cobalt which it contains will be thrown down as protoxide, and this by further treatment with chlorine may be made to yield another portion of sesquioxide, and so on by repeating the operations until the cobalt has been wholly obtained in the state of sesquioxide. An easier method of obtaining the whole amount of cobalt in the condition of sesquioxide consists in using a solution of alkaline hypochlorite instead of free chlorine.

ZINC.

Equivalent or atomic weight . . .	32·6
Specific gravity . . .	from 6·86 to 7·20

Zinc is not very widely diffused over the world, but in the localities which contain it the metal is abundant. It is found principally in two states, the carbonate (*calamine*) and sulphuret or zinc blende. Of these the carbonate is melted with the greater ease, and the zinc produced is of the better quality. In the production of zinc from

calamine the ore is first roasted, for the purpose of driving off water and carbonic acid; it is then reduced by the conjoined agency of heat and contact with carbonaceous material; powdered coke being employed in practice for this purpose. Inasmuch, however, as zinc is a metal of great volatility, the process of smelting differs from that ordinarily followed in the case of other metals. It is raised in vapour and distilled; the distillatory apparatus being a crucible having a luted cover, and furnished with an earthenware pipe through its bottom; the other end of the pipe terminating over a dish of water, as represented in the accompanying diagram. This process of distillation was termed by the older chemists *Distillatio per descensum.*



The colour of zinc is bluish-white. Its physical properties differ remarkably, according to the degree of heat to which it is raised. When cast into an ingot, and allowed to cool to the ordinary atmospheric temperature, zinc is a somewhat brittle metal, and breaks under the shock of the hammer. Between 250° and 300° Fah. it is malleable, and may be reduced to the form of sheet by rolling, thus rendering it so valuable as a substitute for lead and tin plate. When the heat is raised to 400° Fah., it becomes so extremely brittle that it may be readily powdered. At 773° Fah. it fuses, and heated to whiteness it volatilises, and may be distilled. Zinc shavings may be ignited by the flame of a candle as readily as strips of paper. They burn with a magnificent white light, and crumble into a flocculent white oxide, to which the alchemists gave the name of *Lana philosophica.*

Zinc, although an easily oxidisable metal, may be exposed to atmospheric agencies for considerable periods, without more than thin surface oxidisation. When heated, its power of absorbing oxygen, either from dry air or aqueous vapour, is greatly increased. Its power of rapidly decomposing aqueous vapour and liberating hydrogen, commences at a temperature only a little above the boiling point of water, 212° Fah.

Zinc is readily attacked by the greater number of acids; more especially hydrochloric and dilute sulphuric acids, both of which dissolve it with evolution of hydrogen. It is also acted upon when boiled with alkaline solutions. All the soluble combinations of zinc are poisonous; vessels of this metal, therefore, cannot with propriety be brought in prolonged contact with articles of food.

Combination of Zinc with Oxygen (*Oxide of Zinc*).—Only one compound of oxygen and zinc is known; it is composed of a single equivalent of each, and is, consequently, the protoxide of zinc. Oxide of zinc is a powerful base, readily uniting with acids, and forming well defined salts.

Preparation.—One method of forming oxide of zinc I have already described; it consists in burning fine shavings of the metal; when a flocculent result, lana philosophica, or pompholix,—which is the oxide, results. Thus prepared, however, oxide of zinc always contains small traces of the free metal. In the hydrated form, oxide of zinc may be thrown down from the solution of any protosalt of zinc by the addition of potash or soda. The hydrate thus produced, however, retains a little of the alkali with much obstinacy.

If the oxide be required in the state of purity, one of the following methods of preparation should be adopted :—(1). Add carbonate of potash or soda to a protosolution of zinc until nothing further precipitates. Collect the precipitate, which is a hydrated carbonate, wash it thoroughly, and drive off its carbonic acid by the application of furnace heat. (2). Oxide of zinc in the state of complete purity may also be obtained by heating nitrate of zinc in a crucible, when the elements of nitric acid being given off pure oxide of zinc remains.

Oxide of zinc is now generated on the large scale as a substitute for white lead employed as a pigment, over which it has the advantage of not blackening by exposure to sulphuretted hydrogen gas and vapours of hydrosulphate of ammonia. It is, nevertheless, deficient in the quality of body, and, to employ a technical phrase, it does not *cover* so well as white lead.

Salts of Oxide of Zinc.—These salts are all of them characterized by a peculiar styptic taste, which assumes its maximum in the sulphate (white vitriol). All are colourless, except the acid which enters into their composition be itself coloured. Their solutions yield with potash, soda, and ammonia, a white precipitate—the hydrated oxide—soluble in excess of the precipitant. Alkaline carbonates and ferrocyanide of potassium also throw down white precipitates, as, in like manner, the hydrosulphates from solutions either acid or neutral; hydrosulphuric acid, however, only effects precipitation from neutral solutions.

Sulphate of Zinc (*White Vitriol*).—This salt is readily produced by effecting the solution of zinc in dilute sulphuric acid, and evaporating the solution until crystals form. They contain seven equivalents of water, of which six are disengaged, when the salt is heated to 212° Fah. Sulphate of zinc is generated on the large scale by an indirect process, the theory of which will be readily intelligible, from zinc blende or the native sulphuret. The material previously reduced to powder is slowly roasted, by which operation a portion of the sulphur entering into its composition is evolved in the state of sulphurous acid, whilst another portion absorbs oxygen from the atmosphere, and becoming sulphuric acid unites with oxide of zinc, also generated by the absorption of oxygen, and thus constitutes sulphate of zinc; which, being soluble, may be extracted by lixiviation, and crystallized by evaporation to the proper extent.

Carbonate of Zinc.—It has already been mentioned that carbonate of zinc occurs native, and is termed calamine. It is a true neutral, or mono-carbonate, having the composition as indicated by the formula ZnO,Co_2. It has never been artificially produced.

Hydro-carbonate of Zinc.—This term has been applied to the hydrated carbonate which falls when solution of an alkaline carbonate is poured into a solution of salt of zinc. Its composition is very peculiar, as will be seen from the subjoined formula, which represents it :—$(2ZnO.\ CO_2 + 3ZnO.HO)$.

Zinc with Sulphur—Sulphuret of Zinc.

Native sulphuret of zinc exists in large quantities. It is termed zinc blende, and is employed as the source of both white vitriol and metallic zinc. Artificially it may be generated either by heating a mixture of zinc filings, or of oxide of zinc (the latter is preferable) with powdered sulphur in a crucible.

Properties.—Native sulphuret of zinc is a translucid, brownish, compact material, crystallizing in forms belonging to the cubic or tessular system. Artificial sulphuret of zinc, prepared by the methods just described, is a yellowish-white powder.

Zinc with Chlorine—Chloride of Zinc.

Preparation.—(1) By transmitting a current of dry chlorine gas through fragments of metallic zinc.

(2) By dissolving zinc in hydrochloric acid, hydrated chloride of zinc results, and this being heated to about 482° Fah., evolves the whole of its water, and is converted into anhydrous chloride of zinc.

Properties.—Chloride of zinc is a white, fusible, highly corrosive liquid, possessing strong antiseptic properties, soluble in alcohol, combining with water with avidity, and not decomposable with a red heat, but evolved in the state of vapour; thus enabling it to be distilled.

General Characteristics of Zinc Salts.—(1) The most striking peculiarity of zinc salts is the colour of the precipitate (white) yielded by hydrosulphates in solutions both acid and neutral, or by hydrosulphuric acid in the latter.

(2) Solutions of potash, soda, and ammonia yield a white precipitate soluble in excess of the precipitant.

(3) Carbonate of ammonia yields a white precipitate soluble in excess of the precipitant.

(4) Carbonates of potash and soda yield white precipitates insoluble in excess of precipitant.

(5) Ferrocyanide of potassium yields a white precipitate insoluble in excess.

CADMIUM.

Equivalent or atomic weight	56
Specific gravity	8·7

This interesting metal is associated with zinc, with which it presents certain analogies. The history of cadmium is curious. In some parts of Germany the drugs and chemicals of apothecaries are examined for the purpose of ascertaining whether they are free from contaminations. In the year 1817, a portion of white vitriol (sulphate of zinc) having being subjected to this ordeal, it was condemned; being contaminated, as was asserted, with arsenic. To this award the owner of the sulphate of zinc demurred, and referred it to Professor Stromeyer for examination; when, instead of arsenic, a new metal, *cadmium*, was discovered. Both cadmium and arsenic give a yellow precipitate on the addition of hydrosulphuric acid:—hence the mistake.

Method of obtaining Cadmium.—Cadmium it has already been mentioned, occurs in combination with zinc; like which it is volatile, and may be distilled. It is considerably *more* volatile than zinc, however, being evolved at a red heat, whereas zinc does not vapourize until the heat is raised to whiteness; this difference between the two will render the process of obtaining cadmium intelligible. The first portions of volatile matter which pass over when zinc ore is distilled in contact with carbonaceous matter, and which, on account of their burning with a brown flame, are called by the technical name of *brown blaze*, contain very little zinc, and are chiefly composed of arsenic and cadmium. It cannot, however, be obtained completely pure by this means, but a moist chemical process has to be adopted. The impure cadmium result is dissolved in dilute nitric or hydrochloric acid, the acid being in slight excess, and a current of hydrosulphuric acid is transmitted, when sulphuret of cadmium is thrown down, which being redissolved in nitric acid, and carbonate of potash or soda added, yields

carbonate of cadmium, and the latter by mixture with charcoal powder, and distillation, evolves metallic cadmium.

Properties.—Cadmium is a soft, white, ductile, and malleable metal, fusible below redness, and more volatile than zinc.

Combination of Cadmium with Oxygen—Oxide of Cadmium.—Only one oxide of cadmium, the protoxide, is known.

Preparation.—Anhydrous oxide of cadmium may be prepared by burning cadmium in oxygen gas, or atmospheric air; or by strongly heating nitrate of cadmium. The oxide in a hydrated condition may be thrown down from any cadmium salt by the addition of soda or potash.

Salts of Oxide of Cadmium.—All colourless acids when united with cadmium-oxide yield colourless salts of cadmium, from which the hydrated oxide may be precipitated by soda or potash; also by ammonia, though an excess of the latter readily dissolves the precipitate. Carbonates of alkalies throw down a white precipitate, which is a true carbonate of cadmium. Hydrosulphuric acid throws down a yellow precipitate, the sulphuret of cadmium; and alkaline hydrosulphates produce the same result. Sulphuret of cadmium is not soluble in excess of the alkaline hydrosulphate, a quality which distinguishes it from the sulphuret of arsenic. The salts of cadmium merit no individual notice.

TIN.

Equivalent or atomic weight . .	=	59
Specific gravity	=	7·3

History and Natural History.—This metal occurs in very few localities, but it there exists in considerable quantities. Tin has been known from periods of very high antiquity; some of our present Cornish stanniferous districts having been worked by the Phœnicians. The purest tin is obtained from Malacca, but large quantities are obtained from the mines and stream-works of Cornwall and Devonshire. How long the Phœnicians enjoyed exclusively this commerce is not easily determined; but in the days of Herodotus the Greeks appear to have been acquainted with the tin countries by name only. They knew that the tin with which they were supplied by the Phœnician merchants came originally from the Cassiterides, the name by which they knew these islands; and Strabo reports them to have been so determined to conceal whence they derived the metal from other nations, that the master of a Phœnician vessel who suspected that a Roman vessel was following him for the purpose of discovering his secret, chose to run his ship ashore and suffer shipwreck rather than permit his track to be discovered. In process of time, however, the Greeks of Marseilles obtained a considerable portion of this trade, and tin was the chief commodity they exported from Britain. In due course the Romans also discovered the tin countries; and some time before the first Punic War, Publius Crassus was sent to make a report on the tin mines, which constituted a branch of commerce between the natives of this island and the Phœnicians and Greeks many centuries before the commencement of the present era. The principal tin ore is the binoxide.

Properties.—In physical appearance tin much resembles silver. It is very malleable, spreading under the hammer into a sheet, but cannot be drawn into a wire. It fuses at about 450° Fahrenheit, and does not tarnish by exposure to the air. Tin readily dissolves in hot hydrochloric acid, hydrogen gas being evolved, and protochlo-

ride of tin remaining in solution. In dilute sulphuric acid it also dissolves, but not readily; strong and hot oil of vitriol dissolves it, with the evolution of sulphurous acid and the formation of sulphate of oxide of tin. The strongest hydrate of nitric acid (monohydrate) does not act upon tin; but if diluted to the slightest extent violent action takes place, copious fumes of nitrous and hyponitrous acid are evolved, and the tin is converted into stannic acid—sometimes called binoxide, or peroxide of tin. Nitro-hydrochloric acid dissolves tin, and yields solution of the perchloride.

Oxides of Tin.

Two of these are well known,—the protoxide and the binoxide, otherwise called the peroxide of tin, or stannic acid.

Protoxide of Tin.

Preparation.—(1) By adding carbonate of ammonia to a solution of protochloride of tin, the white hydrate of the protoxide of the metal is thrown down; and if this be boiled, its water of hydration is evolved, and it changes to the black anhydrous protoxide. The protoxide generated by this operation rapidly attracts oxygen by exposure to air, and is converted into binoxide.

(2) By adding caustic potash, or soda, to solution of protochloride of tin, a white compound, is formed of the hydrated oxide and the alkali. Boiling decomposes this compound, and generates anhydrous black protoxide of tin; which, unlike that prepared by the operation last described, is stable in the air at ordinary temperatures. Flame ignites it, however; when it burns vividly, and is converted into peroxide.

(3) If ammonia be added to protochloride of tin, the mixture boiled and evaporated, decomposition ensues, and protoxide of tin is thrown down in the condition of red powder.

Hydrated protoxide of tin acts the part of a feeble acid, and combines with various bases, especially the fixed alkalies.

Binoxide, or Peroxide of Tin (Stannic Acid).

Strictly speaking there are two isomeric modifications of this compound; both are sometimes comprehended under one name, but occasionally are distinguished as *stannic*, and *metastannic* acid. Stannic acid is prepared by treating metallic tin with strong nitric acid; metastannic acid is generated by the addition of water to perchloride of tin, when decomposition ensues and metastannic acid is deposited. Native binoxide of tin is the metastnanic acid variety. Both stannic and metastannic acids, after ignition, yield the same result, which may be distinguished by the name of peroxide of tin; it is a lemon-yellow powder, having acid properties, and combining readily with alkalies.

Chlorides of Tin.

There are two chlorides of tin,—the protochloride and the perchloride.

Protochloride of Tin.

Preparation.—By dissolving tin in hydrochloric acid, solution of protochloride is obtained; and by evaporating the latter, a crystalline hydrate of the protochloride is generated, holding 3 equivalents of water. Anhydrous protochloride of tin is generated by distilling a mixture of calomel and powdered tin.

Perchloride or Bichloride of Tin.

Preparation.—(1) By transmitting a current of dry chlorine over powdered tin

until absorption of the chlorine no longer takes place, adding a little powdered tin to the result, for the purpose of removing free chlorine and distilling.

(2) By distilling one part of powdered tin and five parts of corrosive sublimate.

Properties.—Bichloride of tin is a thin colourless liquid. It was known to the alchemists, and called "fuming liquor of Libavius." Heated to 248° Fah. it boils, and sublimes. The density of this substance is 2·28, and the density of its vapour is 9·2. It has a great tendency to unite with water and form hydrates, one of which is crystallisable, and holds five equivalents of water; consequently its formula is $SnCl_2 + 5HO$. When heated, per-chloride of tin is decomposed, hydrochloric acid being evolved, and metastannic acid remaining.

Tin with Sulphur—Sulphurets of Tin.

Two combinations of sulphur with tin are known,—the *protosulphuret* and the *bisulphuret.*

Protosulphuret of Tin.

Preparation.—(1) A mixture of tin filings with sulphur is heated in an earthenware crucible when combination ensues, but the result contains excess of tin. To free it from this it is powdered, mixed with a further amount of sulphur, and again exposed to heat.

(2) Protosulphuret of tin, in the hydrated condition, is formed when a current of hydrosulphuric acid is passed through a solution of protochloride of tin.

Properties.—Anhydrous protosulphuret of tin is a gray, crystalline body. The hydrated protosulphuret is a dark brown, almost black powder.

Bisulphuret or Persulphuret of Tin.

Preparation.—Bisulphuret of tin (hydrated) is the yellow result of transmitting hydrosulphuric acid through a solution of perchloride of tin. If instead of hydrated perchloride of tin, vapours of the anhydrous substance be transmitted through a porcelain tube, heated to dull redness, along with hydrosulphuric acid, *anhydrous* perchloride of tin results in the form of yellow crystalline scales. This material is called *aurum musivum*, or mosaic gold, and is of frequent application in the arts. When prepared on the large scale, however, the following process is adopted :—an amalgam of 12 parts of tin and 6 parts of mercury is intimately mixed with 7 parts of flower of sulphur and 6 parts of sal ammoniac. The mixture is heated in a long-necked flask by means of a sand bath, up to the temperature of dull redness. Portions of sulphur and of sal-ammoniac, sulphuret of mercury, and protochloride of tin are evolved, leaving the pure bisulphuret of tin in the flask. The use of the sal-ammoniac employed in this operation is to prevent, by its evaporation, a too great elevation of temperature.

Characteristics of Salts of Tin.—General remarks. Both oxides of tin act the double part of acids and bases, but the acid quality, even of the protoxide of tin, predominates. Solutions of tin may, therefore, come under the notice of the chemists as protosolutions and persolutions, and these may again be sub-divided into tin-acid and tin-basic.

Special Characteristics of Protosolutions of Tin.—Of this class of bodies, solution of protochloride may be taken as the most convenient type—it illustrates the following characteristics :—

(1) Solutions of caustic potash and soda yield a white hydrate of the oxide soluble in excess of the precipitant.

(2) Ammonia and its carbonate, also carbonates of the fixed alkalies, yield a white hydrate of the oxide, *insoluble* in excess of precipitant.

(3) Hydrosulphuric acid, and the hydrosulphates, yield a black precipitate,—the hydrated protosulphuret of tin.

The preceding remarks are common to all soluble protosalts of tin, in addition to which the protochloride has two remarkable characteristics of its own; mixed with chloride of gold it yields a purple precipitate, much used in the art of porcelain painting, and known as the *purple powder of Cassius*, and added to a salt of mercury it reduces the latter to a lower degree of oxygenation, or takes from it all the oxygen, yielding metallic mercury according to the nature of the mercury salt and the quantity of protochloride employed. Thus, if bichloride of mercury (corrosive sublimate) be the subject of experiment, it is first reduced to calomel (protochloride), and this latter is finally reduced to the condition of metallic mercury.

Special Characteristics of Persalts of Tin.

(1) The caustic fixed alkalies throw down a white hydrate, soluble in excess of the precipitant.

(2) Ammonia throws down the same hydrate, but insoluble in excess of precipitant.

(3) Solutions of carbonated fixed alkalies throw down a white hydrate, slightly soluble in excess of precipitant.

(4) Solution of carbonate of ammonia throws down a white hydrate, insoluble in excess of precipitant.

(5) Hydrosulphuric acid throws down a yellow precipitate, the hydrated bisulphuret; insoluble in excess.

(6) The alkaline hydrosulphates throw down the same hydrated bisulphuret; soluble in excess of precipitant.

Remarks.—The yellow colour of the precipitate thrown down from solutions of the bichloride of tin by hydrosulphuric acid and the hydrosulphates merits especial attention, as being of a similar colour to the precipitate yielded by arsenical solutions treated in the same manner. Two metals only of those which have already come under our notice furnish yellow precipitates, with hydrosulphuric acid and the hydrosulphates. They are cadmium, and tin in the state of perchloride, and some other forms of percombination. Hereafter it will be seen that solutions of arsenious acid also furnish a yellow precipitate, with the same re-agents. Some chemists include antimony in the list of metals which afford a yellow precipitate, with hydrosulphuric acid and the hydrosulphates. Strictly speaking, however, the tint of this latter is orange-red; but inasmuch as it may count for yellow in certain coloured solutions, we may as well include antimony in the list of metals furnishing yellow precipitates with hydrosulphuric acid and the hydrosulphates.

TITANIUM.

Equivalent or atomic weight	25
Specific gravity	?

This metal is found in nature as a constituent of titaniferous iron, and in the form of a mineral called *rutile*, which latter is titanic acid almost pure; it exists, moreover, in several other minerals, but in small quantity.

Preparation.—Metallic titanium may be obtained in the laboratory by heating the perchloride of titanium in a glass flask, and passing into it a current of ammoniacal gas. The ammonia combines with the perchloride of titanium, and forms a pulverulent substance. The flask now being surrounded with burning charcoal, sal-ammoniac sublimes, and metallic titanium remains in the form of little globules.

Properties.—Titanium, thus prepared, is somewhat easily attacked by acids, whereas titanium which occurs as a casual result in iron-smelting furnaces, is not.

Combinations of Titanium with Oxygen.—Of these bodies three are known; the protoxide, sesquioxide, and titanic acids. Their respective composition is as follows:

Protoxide of titanium	$Ti\,O$
Sesquioxide	$Ti\,O_3$
Titanic acid	$Ti\,O_2$

Of the preceding bodies, titanic acid is the most important.

Preparation.—Pulverised titanite having been mixed with carbonate of potash and fused, the result is treated with water, by which means all excess of alkali is removed. The residue is now dissolved in hydrochloric acid mixed with water and boiled, when titanic acid precipitates.

Properties.—Titanic acid is a white powder, soluble in acids, with which, however, it does not form permanent salts, the acid solutions being decomposed by boiling, as we have seen already in the preparation of titanic acid. These characteristics of titanic acid—namely, its solubility in acid when freshly prepared—but easy decomposition of the acid solution, assimilate titanic acid to silica.

Protoxide of Titanium.

When titanic acid is strongly heated in a charcoal-lined furnace it loses oxygen, and is converted into a black powder, which chemists for the most part regard as protoxide of titanium.

Sesquioxide of Titanium.

When titanic acid is strongly heated in a current of hydrogen gas it is converted into a black powder, which is considered to be sesquioxide of titanium. This oxide in a hydrated condition precipitates, when ammonia is added to a solution of the sesquichloride of the metal.

Titanium and Chlorine—Chlorides of Titanium.

Two chlorides of titanium are known; the sesquichloride corresponding with the sesquioxide, and the bichloride, which corresponds with titanic acid, and which is, therefore, the bichloride.

Perchloride of Titanium.

Preparation.—An intimate mixture is effected of titanic acid and carbonaceous matter, the whole is placed in a tubulated retort, and a current of dry chlorine gas is liberated upon the mixture, heated by means of a tube passing through the tubulure of the retort; a full red heat is necessary for conducting the operation. Chloride of titanium passes over in the condition of a volatile colourless liquid, and must be condensed in a receiver, surrounded by a freezing mixture. It combines violently with water, behaving like the bichloride of tin similarly treated.

Sesquichloride of Titanium.

Preparation.—By transmitting hydrogen, saturated with the vapour of bichloride of titanium, through a red-hot porcelain tube.

Properties.—A crystalline violet-tinted material, very deliquescent, and forming a violet or red solution with water. The most prominent characteristic of the sesquichloride of titanium is its powerful reducing quality. It precipitates gold, silver, and mercury from their solutions in the metallic state, and reduces copper solutions to the minimum state of oxydation. In like manner, it decomposes sulphurous acid with the liberation of sulphur. This latter agency is especially remarkable, sulphurous acid itself being a powerful reducing body, separating oxygen from many substances, and employed practically for the purpose in question.

General Characteristics of Titanium and its Compounds.—The similarity which titanic acid bears to silica has already been pointed out; in certain respects titanium bears a relationship to tin, as will be seen on a comparison of the stanniferous with the titaniferous compounds. The two, however, admit of being readily distinguished by the following blowpipe characteristics:—Tin compounds, when mixed with charcoal and carbonate of soda, and heated in the blowpipe flame, yield metallic tin; whereas titanium compounds mixed with borax, and heated in the oxidising part of the blowpipe flame, yield a colourless glass, becoming at once blue when acted on by the reducing flame.

TANTALUM, TANTALIUM, OR COLUMBIUM, NIOBIUM, ILMENIUM, AND PELOPIUM.

These metals are amongst the curiosities of mineral chemistry; very little concerning them is known, and they have hitherto been procured in quantities so small that the study of their chemical relations is very incomplete.

Tantalium was discovered by Mr. Hatchett in 1801, in a mineral brought from America; he therefore gave the name of Columbium to the extracted metal. In the year 1802, the Swedish chemist Ekeberg rediscovered the metal in a Swedish mineral, not being aware of what Hatchett had accomplished. Subsequently, Dr. Wollaston proved tantalium and columbium to be identical.

Niobium and Pelopium were both discovered by Heinrich Rose in the year 1846, and Ilmenium by Herrmann in 1847. All these metals are found associated with tantalium, in the Swedish mineral *yttro-tantalite.*

LEAD.

Equivalent or atomic weight . . .	103·7
Specific gravity	11·445

It is unnecessary to state that lead is a very useful and abundant metal, that it is largely used in the arts and manufactures, and extracted from its ores with facility. Commercial lead, however, is never pure; a very general impurity being silver, besides which there are others. The presence of portions of silver in lead too inconsiderable to render its extraction remunerative, materially lessens the value of lead for many purposes, more especially those of gold and silver assaying, in the course of which pure lead is employed, as will be seen hereafter, when these metals are treated of.

Preparation of Lead (chemically pure).—When crystallized nitrate of lead is decomposed by heat, pure oxide of lead remains, and the latter if mixed with charcoal and sugar into a paste, dried, and heated in a crucible lined with charcoal yields pure metallic lead.

Properties.—The physical properties of lead are well known, amongst which its softness is most conspicuous. In proportion as lead is unmixed with other metals, so is it more soft. The malleability, ductility, and ready fusibility of this metal are so well known, that these properties require no comment. The temperature at which lead fuses is about 635° Fah.

Lead, when absolutely clean, is a somewhat brilliant metal, but it easily tarnishes by exposure to atmospheric influences; becoming covered with a superficial layer of oxide, and oxide mixed with carbonate of lead. This change is greatly facilitated by the conjoined agency of moisture and carbonic acid. The superficial crust of lead oxide formed under these circumstances has been much studied, in relation to the action upon it of water. Pipes of lead, and cisterns of that metal, are so commonly employed for the conveyance and retention of water, that it is eminently necessary to determine the conditions under which their employment is safe, or the contrary. The following is a summary of the chief facts which have been made out in relation to this subject:—Water absolutely pure, that is to say, free from air as well as solid impurities, does not dissolve lead. Such is the expression of a chemical fact; but the conditions are almost impracticable. They may be secured for the purposes of demonstration, but do not admit of being applied in practice, inasmuch as water no sooner comes in contact with atmospheric air than a portion of the latter is dissolved, when the water thus charged attacks lead with facility, as may be demonstrated by steeping a piece of lead in distilled water, when speedily the liquid will be found to contain traces of lead by the evidence of tests for that metal,—more especially hydrosulphuric acid. If, however, instead of pure water charged with atmospheric air, water holding a little saline matter be employed, its power of dissolving lead will be found either to have vanished altogether, or to have much diminished, according to the quantity and the nature of the impurities in question. Practically, then, the deductions are these:—Distilled water must on no account be passed through leaden pipes or stored in leaden cisterns; neither must rain water, approaching, as it does, more nearly to the condition of absolute purity than any other kind of water naturally existing. River water may generally be brought into prolonged contact with lead without fear of danger, and so, in the majority of instances, may spring water; but there are exceptions. Some kinds of spring water are so remarkably free from contaminations that they act upon lead. Before adopting lead to the purposes of water retention, it is well to try the effect of steeping lead in a portion of the water during some days, and testing the fluid for lead. In all cases involving the solution of lead by water, the process of solution goes on at the line of the water level, and, consequently, at the line where air and water simultaneously act.

Combinations of Oxygen with Lead—Oxides of Lead.

Three combinations are known of oxygen with lead. They are the *suboxide*, the *protoxide*, and the *binoxide*. The latter is sometimes denominated *plumbic acid*. In addition to these oxides, the binoxide, as acid, combines with the protoxide as base, and forms one or more intermediate oxides, or rather lead salts.

Suboxide of Lead.

Preparation.—By heating oxalate of lead, at a temperature of about 570° F., until no further gas is disengaged. In some chemical treatises the suboxide of lead is considered to be a mixture of metallic lead and protoxide of the metal, an opinion which

cannot be reconciled with the fact that quicksilver triturated with the oxide does not dissolve the smallest particle of lead, which it would do if the latter existed. Its composition is indicated by the formula Pb_2O.

Protoxide of Lead.

Preparation.—(1) By calcining the nitrate or the carbonate of lead.

(2) By adding solution of ammonia to a solution of any protosalt of lead.

The result of the first operation is anhydrous protoxide of lead, that of the second operation is usually hydrated oxide of lead; but if, after the addition of ammonia, the solution be evaporated, protoxide of lead separates in the anhydrous condition.

Properties.—Hydrated protoxide of lead is a white powder; anhydrous protoxide of lead is either red or yellow, according to the temperature at which it has been prepared. Anhydrous protoxide of lead is produced on the large scale, and applied to many purposes in the arts and manufactures. When completely fused it is called litharge, but when the heat employed in generating it has been less intense, so that it remains pulverulent, the term massicot is applied. Protoxide of lead, though readily uniting with acids, and forming well-defined salts, is itself an acid; readily combining with potash, soda,—even ammonia, and many of the earths, more especially baryta, strontia, and lime. Its composition is indicated by the formula PbO.

Binoxide of Lead, or Plumbic Acid.

Preparation.—(1) By digesting minium, or red lead, which may be denominated chemically *plumbate of protoxide of lead*, with weak nitric acid, when protoxide of lead is dissolved, protonitrate of lead formed, and binoxide of lead isolated.

(2) By transmitting a current of chlorine through protoxide of lead suspended in water.

(3) By pouring an alkaline hypochlorite into a boiling solution of acetate of lead.

The second and third of these processes yield binoxide of lead simultaneously with a variable portion of chloride of lead; and the latter, as we shall presently learn, is a somewhat insoluble substance. Hence, the binoxide of lead prepared by either of these processes must be copiously washed with boiling water, to effect the removal of the chloride.

Properties.—A puce-coloured powder, which does not combine with acids, thus demonstrating the absence of basic quality, but which readily combines with potash, soda, lime, baryta, strontia, and some other bases, forming, in many cases, well-defined crystalline salts. The most leading characteristic of binoxide of lead is dependent upon the facility with which it yields up oxygen to substances having an affinity for that element. For example, if mixed with an aqueous solution of sulphurous acid or the dry gas, it at once converts the latter into sulphuric acid, and is itself reduced to protoxide of lead, which immediately combining with the sulphuric acid generated, forms sulphate of protoxide of lead. By this means sulphurous acid may be separated from other gases.

Salts containing Protoxide of Lead as Base—Sulphate of Lead.

Preparation.—Dilute sulphuric acid does not act upon lead, either hot or cold, but concentrated sulphuric acid, when boiled with lead, first converts the metal into protoxide with the liberation of sulphurous acid, and finally unites with the protoxide, giving rise to sulphate of protoxide of lead, more usually designated *sulphate of lead.*

Sulphate of lead may also be generated by the addition of sulphuric acid, or a soluble sulphate to any protosalt of lead.

Properties.—A white powder, nearly insoluble in water, but slightly soluble in acid liquors, especially such as contain sulphuric acid. Boiling hydrochloric acid decomposes it, and generates chloride of lead. Sulphate of lead cannot be decomposed by heat alone, but if ignited in contact with carbonaceous matter, in close vessels, it loses oxygen and becomes sulphuret, or sulphide of lead. Sulphate of lead, diffused through water slightly acidulated with sulphuric acid, is at once decomposed by contact with iron or zinc: boiling solutions of carbonate of potash, or of soda, also decompose it, with the formation of carbonate of lead, and sulphate of the alkali.

Nitrate of Lead.

Preparation.—By digesting litharge with nitric acid, or by acting upon metallic lead with the same acid. In either case the acid must be in excess, otherwise a basic or subnitrate of lead is formed; the tendency to generate basic or subsalts being a characteristic of the protoxide of lead. The solution obtained, as described, being evaporated and set aside to crystallize, deposits crystals of nitrate of lead.

Acetates of Lead.

There exist several acetates of lead; one neutral, and the remainder basic, or subacetates.

Neutral Acetate of Lead.

Preparation.—By boiling litharge with dilute acetic acid (vinegar), taking care that the acid be always in excess; and crystallizing by slow evaporation. Crystals of acetate of lead contain three equivalents of water; hence their composition is expressed by the formula $PbO. C_4H_3O_3 + 3HO$.

Properties.—Acetate of lead has a sweet taste, hence the popular name *sugar of lead.* It readily dissolves in water, and its solution exposed to the air absorbs carbonic acid, giving rise to the formation of carbonate of lead. Crystals of acetate of lead evolve the whole of their water in vacuo, and also when heated to 212° F.

Subacetates, or Basic Acetates of Lead.

The best known of these bodies, as also the most important, is the tris, or triacetate, formed by dissolving neutral acetate of lead in water, and boiling the solution with an amount of litharge equal to the weight of oxide contained in the original acetate. The formula of this acetate is $3PbO. C_4H_5O_3 + HO$. When dissolved in water it constitutes the well-known *Goulard's Extract*, employed in surgical and medical practice.

All the acetates of lead, but more especially the basic acetates, have the property of combining with certain vegetable colouring matters, and forming somewhat insoluble precipitates. A good illustration of this property is furnished by common yellow or muscovado sugar. If this substance be dissolved in water, the solution heated to about 120° F., and Goulard's solution added, a dense flocculent precipitate forms; and the sugar remaining in solution is almost freed from colouring matter; but it is still contaminated with lead. The latter, however, may be effectually separated, even on a large scale, by a stream of sulphurous acid. Taking advantage of this property, I some years since introduced subacetate of lead as a purifying agent in sugar refineries, using sulphurous acid to remove all excess of lead.

Chloride of Lead.

Preparation.—By adding hydrochloric acid, or any soluble chloride, to a soluble salt of lead; or by digesting protoxide of lead with hydrochloric acid.

Properties.—A white powder, somewhat crystalline, soluble in 135 parts of cold water, but considerably more soluble in hot water.

Carbonate of Lead, or White Lead.

This important substance is well known, owing to its employment as a white pigment. Notwithstanding its quality of becoming black by exposure to atmospheres containing hydrosulphuric acid or hydrosulphate of ammonia, and the dangerous results of handling it continuously, no other preparation has been found competent to take its place.

Carbonate of lead may be readily made by bringing a solution of acetate of lead in contact with a soluble carbonate, or gaseous carbonic acid, pure or mixed. On the large scale, there are several processes of manufacturing it, which the limits of this volume will not permit me to describe.

General Characteristics of Lead Salts.

Sulphuric acid, or soluble sulphates, throw down a white precipitate, *quite insoluble in water*, sulphate of lead, the qualities of which have already been described.

Hydrochloric acid, or solution of chloride, throw down the chloride of lead nearly insoluble in cold water.

Hydrosulphuric acid and hydrosulphate of ammonia throw down a black precipitate.

Iodide of potassium throws down the yellow iodide of lead.

Soluble chromates and bichromates throw down the yellow chromate of lead.

Ammonia, carbonate of soda, potash, and ammonia, all throw down a white precipitate insoluble in excess.

BISMUTH.

Equivalent or atomic weight	213
Specific gravity	9·9

Properties—A crystalline metal, white, but with a certain tendency to redness, and fusing at about 510° Fah. Bismuth is not affected by exposure to dry atmospheric air; but if the air be moist, its surface slowly oxidises. Nitric acid is its best solvent; hydrochloric and sulphuric acid attack it only when hot, and even then with difficulty.

Bismuth and Oxygen—Oxides of Bismuth.

Three combinations of oxygen with bismuth are known; their composition is as follows:—

	Bismuth.	Oxygen.
Oxide of bismuth	2	3
Peroxide of bismuth, or bismuthic acid . . .	2	5
Intermediate oxide, a compound of bismuthic acid with oxide of bismuth	4	8

Oxide of Bismuth.

The per-centage composition of oxide of bismuth is as follows:—

Bismuth	89·86
Oxygen	10·14
	100·00

Some chemists regard it as a compound of one equivalent of bismuth plus one equivalent of oxygen; but this assumption does not accord with the analogies of the oxide.

Preparation.—(*a*). *Anhydrous Oxide.*—(1) By heating the metal in contact with oxygen or atmospheric air. (2) By heating one of the basic nitrates of bismuth. (3) By boiling the hydrated oxide next to be described with solution of potash.

(*b*). *Hydrated Oxide.*—By adding solution of potash, soda, or ammonia, to one of the basic or subnitrates, and *not* heating the mixture; otherwise the anhydrous oxide (see above) will be generated.

Properties.—Anhydrous oxide of bismuth is yellow; hydrated oxide white.

Salts of the Oxide of Bismuth.

The most important of these, and the only ones of which we need take cognizance here, are the neutral nitrate of bismuth, and the basic or sub-nitrates of bismuth, its derivatives.

Nitrate of Bismuth (neutral).

Preparation.—By digesting metallic bismuth, or its oxide, with nitric acid, and evaporating.

Properties.—A colourless crystalline deliquescent body, having the composition of $Bi_2O_3\ 3\ NO_5 + HO$. It may be dissolved in a small quantity of water; but when the amount of water added is considerable, it decomposes into a solution which contains oxide of bismuth combined with excess of nitric acid, and which is consequently a supernitrate, and a white precipitate which contains oxide of bismuth, with less nitric acid than is found in the neutral nitrate; hence it is a *sub* or *basic* nitrate of bismuth. The exact composition of the resulting super and subnitrate of bismuth varies according to the relative amount of water added. One of the subnitrates of bismuth (the trisnitrate) is used in medicine, and the subnitrates generally are employed as cosmetics. They possess the disadvantage, however, of blackening by exposure to hydrosulphuric acid or the hydrosulphates.

The peroxide of bismuth, or bismuthic acid, merits but slight attention: it is prepared by transmitting chlorine through potash solution in which hydrated oxide of bismuth is suspended, or, still better, adding solution of hypochlorite of soda to the hydrated oxide, and boiling. Peroxide of bismuth is a brown powder, not capable of uniting with acids.

General Characteristics of Salts of Bismuth.

(1) Decomposition by the addition of water.—We have already seen that the addition of water to nitrate of bismuth decomposes the salt into supernitrate, and subnitrate. All salts of bismuth participate in this quality, thus furnishing the most striking characteristic of the metal; not that bismuth stands alone in this respect, but it furnishes the most conspicuous example.

(2). Hydrosulphuric acid, and hydrosulphates throw down a black precipitate not soluble in excess.

(3). Alkalies and their carbonates yield white precipitates insoluble in excess of precipitant.

(4). Copper, iron, or zinc immersed in a solution of bismuthic salt, throw down metallic bismuth as a black powder.

ANTIMONY.

Equivalent, or atomic weight . . .	129
Specific gravity	6·8

This important metal is chiefly found in nature as a sulphuret, though not pure. The commercial designation of native sulphuret of antimony is simply *antimony*, whereas antimony in a chemical sense is termed in commercial language *regulus of antimony*.

Properties.—Antimony is a white, crystalline, exceedingly brittle metal; it melts at a heat below redness, volatilizes at a white heat, and has a specific gravity of about 6·8. It may be exposed to cold atmospheric air, moist or dry, without oxidation, but when strongly heated it crumbles into oxide. Nitric attacks it energetically, binoxide of nitrogen being liberated, and antimonic acid (a white powder) remaining.

Combinations of Antimony with Oxygen—Oxides of Antimony.

Three of these compounds are known: oxide of antimony, antimonious, and antimonic acids. Many chemists regard the second as a combination of the first and third. The per centage composition of these oxygen compounds is well determined; but chemists are not agreed as to their exact atomic constitution. Some consider oxide of antimony to be composed of two equivalents metal plus three of oxygen, and to be represented by the formula $Sb_2 O_3$; others believe the amount of antimony combined with the three of oxygen to represent one atom. Similarly, antimonic acid may be regarded as composed of $Sb_2 O_5$ or $Sb O_5$, and antimonious acid may be regarded as $Sb_2 O_4$ or $Sb O_4$. I shall adopt the latter of these hypotheses—not as being necessarily the correct one, but as being the more convenient.

Oxide of Antimony—($Sb_2 O_3$).

Preparation.—(1) By projecting powdered antimony into a large crucible heated to redness, when brilliant crystals of oxide of antimony are produced, but they are liable to be contaminated with antimonious acid. A better process is the following:—

(2) By pouring gradually, and in small portions, chloride of antimony into a boiling solution of carbonate of soda. Crystalline anhydrous oxide of antimony is by this treatment thrown down.

Properties.—A grayish-white substance, which fuses at a red heat, and volatilizes at a heat short of full whiteness. When heated in contact with atmospheric air, or oxygen gas, it absorbs the latter and becomes raised to the condition of antimonious acid. Oxide of antimony, notwithstanding its containing the minimum of oxygen, is rather acid than basic: it readily unites with potash and soda, forming true salts, which, however, do not admit of crystallization. Both sulphuric and nitric acid combine with oxide of antimony in several proportions, but the resulting salts are very unstable, and have not been much studied. The most important compound is tartar emetic (tartrate of antimony and potash), much used as a therapeutic agent. Tartar emetic may be diluted with water to any extent without decomposition, and it is almost the only compound of oxide of antimony to which the remark applies.

Antimonious Acid—($Sb O_4$).

Preparation.—By projecting powdered antimony into a large crucible, heated to

redness as in the preparation of oxide of antimony; but continuing the operation longer.

Properties.—A dirty white powder, not volatile, and infusible. When recently prepared it slightly dissolves in water and in acids, but not otherwise. It combines with alkalies, but does not yield well-characterized salts. From its alkaline solutions it falls as a hydrate on the addition of acids.

Antimonic acid, A *and* B.

Under the general designation of antimonic acid, two isomeric bodies were long included; they are now distinguished as *antimonic* and *meta-antimonic acids.* In this respect antimonic acid resembles *phosphoric* and *stannic* acids.

Antimonic Acid, A.

Preparation.—When strong nitric acid is poured upon metallic antimony, a violent action takes place, binoxide of nitrogen being evolved and antimonic acid combined with water (hydrated), and perhaps mixed with some nitric acid remaining. If this hydrated product be heated, anhydrous antimonic acid results.

Properties.—A yellowish-white powder, which decomposes when heated to redness; oxygen being evolved and antimonious acid remaining. Antimonic acid can be made to unite with bases, generating a class of salts termed antimonates, all of which are decomposed by mixture with almost any acid, hydrated antimonic acid being thrown down. Two antimonates of potash are known, the mono- and the bi-antimoniate. Neutral salts of this acid contain one equivalent of base.

Antimonic Acid, B—*Meta-antimonic Acid.*

Preparation.—By decomposing perchloride of antimony by the addition of water. The antimonic acid thrown down by this treatment is hydrated. If it be heated short of redness, the water of hydration is evolved, and anhydrous antimonic acid, similar in all respects to that just described, is obtained. Hence it appears that the distinctive characteristics of antimonic and meta-antimonic acid only refer to the hydrated substances. Meta-antimonic acid forms neutral salts with two equivalents of base.

Antimony with Hydrogen.

This is a compound of great importance, though its atomic constitution is not known, inasmuch as it has never been obtained pure. The great interest of antimoniuretted hydrogen depends on the circumstance that arsenic also combines with hydrogen, forming a compound similar in many respects to antimoniuretted hydrogen, and therefore liable to be confounded with it by an inexperienced operator. Antimoniuretted hydrogen is generated whenever hydrogen gas is developed in a liquid holding antimony in solution. It is a colourless gas, combustible like hydrogen, and during the act of combustion deposits a crust of metallic antimony. Although the general similarity of this antimonial crust to a deposition of metallic arsenic has led to mistakes, they are wholly inexcusable; one characteristic is alone sufficient to distinguish the two metallic depositions; it is this: the antimonial crust is almost incapable of volatilization by the heat of a spirit-lamp flame, whereas the arsenical crust volatilizes readily under this treatment. There are other more elaborate characteristics of distinction between the two, but the one mentioned is in most, if not *all*, cases sufficient.

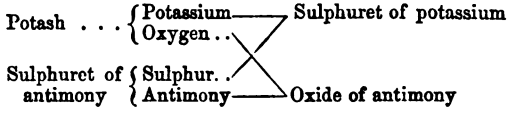
Antimony with Sulphur—Sulphurets of Antimony.

Two of these sulphurets are known; they may be distinguished as the native sulphuret and sulpho-antimonic acid.

Native Sulphuret, composition $Sb\,S_3$.—A gray metallic brittle substance, easily fusible and crystalline; it constitutes the only antimonial ore. Sulphuret of antimony having this composition may be also artificially prepared, either by melting together sulphur and antimony in due proportions, or by transmitting hydrosulphuric acid gas through solution of tartar emetic. When generated by the last process, sulphuret of antimony is orange-red; but in composition it is identical with the other variety. By some it is described as a hydrated sulphuret, but the water seems to be a casualty; it may be totally expelled by application of gentle heat, leaving the sulphuret still red; but if the heat be still raised the sulphuret turns black, like the native variety, and the variety prepared by fusing together sulphur and metallic antimony.

The change which ensues when sulphuret of antimony is roasted, or strongly heated with a current of atmospheric air playing over it, is peculiar. Most sulphurets, when treated in this manner, either yield sulphurous or sulphuric acids, or both, by the oxidation of sulphur; whilst the metal of the sulphuret, simultaneously oxidising, forms an oxide, which combines with sulphuric acid generated, yielding a sulphate. When sulphuret of antimony is strongly roasted, a portion of sulphur escapes uncombined, and a portion of oxide of antimony is formed; subsequently the oxide and sulphuret of antimony combine, forming an oxysulphuret, which fuses into a hard yellowish-red vitreous body. Oxide and sulphuret of antimony combine in many proportions, forming many oxysulphurets.

When sulphuret of antimony is boiled with caustic or carbonated alkalies it is dissolved; and, by virtue of certain decompositions, to be presently explained, oxide of antimony is first deposited on cooling, and afterwards red, sulphuret of antimony. The latter was termed by the older chemists *Kermes mineral.* The decompositions which ensue on boiling sulphuret of antimony with caustic, or carbonated alkaline solutions, are as follow:—Firstly, double decomposition takes place between the alkali (we will assume it to be potash) and a portion of sulphuret of antimony, sulphuret of potassium being formed and oxide of antimony thrown down, as represented by the accompanying diagram;—



Of these bodies, the sulphuret of antimony remains in solution, and the oxide of antimony deposits; but on concentrating the solution by boiling, the sulphuret of potassium combines with a portion of undecomposed sulphuret of antimony, from which a portion of the latter separates in cooling, in the form of Kermes mineral. If to the hot solution, holding sulphuret of antimony and sulphuret of potassium, hydrochloric acid be added, a mixture of oxide and sulphuret of antimony is thrown down, constituting the oxysulphuret of antimony of the English pharmacopœia.

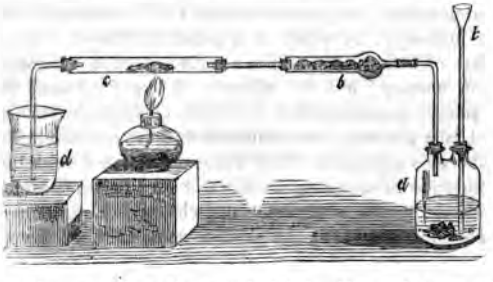
SULPHOANTIMONIC ACID.

This sulphuret of antimony, the composition of which is indicated by the formula $Sb\,S_5$, is generated by transmitting a current of hydrosulphuric acid through a solution of perchloride of antimony in dilute hydrochloric acid, when it precipitates as a yellow powder. It may be generated also by the following process:—Boil a mixture of 18 parts of finely-powdered sulphuret of antimony, 17 of dry carbonate of soda, 13 parts of lime previously slaked, and 3½ parts of sulphur, in sufficient water to reduce the whole to the condition of thin gruel; by which treatment carbonate of lime, antimonate of soda, sulphuret of sodium, and sulphuret of antimony are formed.

Of these bodies, the first is insoluble, the second very nearly so.* By evaporating the solution to a certain extent and allowing it to cool, they may be separated whilst the two sulphurets combine together, and form an antimonio-sulphuret of sulphuret of potassium, which may be obtained in crystals. If a solution of this double sulphuret be mixed with dilute sulphuric acid, decomposition ensues, and pentasulphuret of antimony, otherwise called sulpho-antimonic acid, is precipitated.

All the sulphurets of antimony, but more especially the sulphuret precipitated from an antimonial solution when hydrosulphuric acid is transmitted through it, may be decomposed by heating it in contact with a current of hydrogen gas; when hydrosulphuric acid is formed, and metallic antimony remains. This operation is of great utility in toxicological investigation, as serving to determine the presence of antimony, without any considerable loss of the metal; but it is seldom eligible as a means of rigid quantitative analysis, in consequence of the tendency of a portion of antimony reduced to combine with the passing hydrogen, and generate antimoniuretted hydrogen gas.

The apparatus employed for effecting the decomposition of sulphuret of antimony, by a current of hydrogen gas, is as represented in the accompanying diagram. *a* represents a Woulfe's bottle, adapted to the purpose of generating hydrogen gas by the contact of dilute sulphuric acid (poured through *t*) with granulated zinc. The hydrogen thus evolved is moist, but on passing through fragments of fused chloride of calcium, in the tube *b*, it is dried. The sulphuret of antimony to be decomposed is thrust into the tube *c*, as represented in the diagram, and subjected to the heat of a spirit-lamp flame, whilst a current of dry hydrogen gas passing over it removes sulphur, forms hydrosulphuric acid gas, and leaves metallic antimony. The collateral formation of antimoniuretted hydrogen already adverted to, not being taken cognizance of, the decomposition which ensues is as follows:—



Hydrogen ——— Hydrosulphuric acid

Sulphuret of antimony { Sulphur / Antimony ——— remains in the tube

* Hence antimonic acid becomes a test for soda.

In the pictorial diagram just given, the tube from which the hydrosulphuric acid gas emerges is seen to pass into a beaker glass *d*, containing a solution,—that solution is acetate of lead, and its purpose is to indicate that the operation is proceeding satisfactorily. Whilst decomposition of sulphuret of antimony proceeds, hydrosulphuric acid continues to be liberated, and of course blackens any soluble lead-salt which may be exposed to it. By changing the lead solution from time to time, we learn when the decomposition has ceased, for no sooner is this point arrived at than the lead solution ceases to be blackened.

Antimony with Chlorine—Chloride of Antimony.

Two chlorides of antimony are known, corresponding respectively with oxide of antimony and antimonic acid. The former may be correctly designated terchloride, and the latter pentachloride of antimony.

Terchloride of Antimony—($Sb\ Cl_3$.)

This useful and long-known compound, known by the designation "*butter of antimony*," may be prepared by various methods.

(1) By transmitting chlorine through a tube containing powdered antimony in excess. The chlorine must be passed very slowly, otherwise pentachloride of antimony would be formed.

(2) By distilling in a glass retort a mixture of 1 part pulverized metallic antimony and 2 parts corrosive sublimate.

(3) By digesting native sulphuret of antimony in hydrochloric acid, and evaporating the solution still containing excess of acid.

Properties.—A white easily fusible compound, capable of being volatilized at a low red heat, and which at ordinary atmospheric temperature assumes the consistence of *fat*, whence the name butter of antimony, by which it is popularly known. Tersulphuret of antimony, like nitrate of bismuth, may have a certain portion of water added to it without decomposition ensuing; but the addition of larger portions of water causes the deposition of a subsalt (a subchloride), by which quality chloride of antimony, and, indeed, antimonial salts generally, are assimulated to those of bismuth. Tartar emetic furnishes almost the only exception. The white precipitated subsalts generated by the dilution of terchloride of antimony with water vary in ponderable composition, according to the relative amounts of water, and chloride of antimony employed in generating them. They are known by the popular name of "powder of Algaroth."

Pentachloride of Antimony—($Sb_2\ Cl_5$).

It has already been stated, that if in preparing the compound just described the chlorine be transmitted too rapidly, pentachloride of antimony is generated. The latter substance is indeed prepared by transmitting chlorine over heated powdered antimony. It is next to impossible so to regulate the operation that some of the terchloride of antimony shall not be simultaneously generated, but the two may be readily separated by distillation; terchloride of antimony, as we have already seen, not being volatile at a heat short of redness, whereas the pentachloride may be distilled from an ordinary glass retort; the first portions, however, which come over always hold a little free chlorine, and should be rejected.

Properties.—Pentachloride of antimony is a liquid almost colourless, and, as we

have seen, easily volatilizable. It undergoes spontaneous decomposition when exposed to the air, and more especially if heated.

Distinctive Characteristics of Antimonial Solutions.

The recognition of the presence of antimony is of especial importance, inasmuch as the metal, owing to its yielding a somewhat yellow (orange) precipitate with hydrosulphuric acid, and to its demeanour with hydrogen, is sometimes confounded with arsenic. The first point to be remembered in searching for antimony in organic solutions, such as the contents of the stomach, for example, is the tendency of most solutions containing the metal to be decomposed by the addition of water, yielding subsalts which precipitate. All these precipitates, without exception, are soluble in tartaric acid; hence it is proper to begin an investigation for antimony, supposed to be present in organic solutions, by addition of tartaric acid; when any subsalts which might have been present will be dissolved, and may now be filtered. The chief characteristics of antimony in solution are the following:—

(1) A current of hydrosulphuric acid, even in acid solutions, throws down an orange-coloured precipitate, which being incorporated with black flux (a mixture of carbonate of potash and carbon, made by projecting a mixture of two parts of cream of tartar and one part of nitre into a large red hot crucible), and strongly heated in a glass tube, yields metallic antimony, *not capable of being perceptibly volatilized by the strongest heat of a spirit-lamp flame.* This last is a very important characteristic, distinguishing antimony from arsenic; the latter metal, as we shall hereafter discover, may be chased from one extremity of a closed glass tube to the other by the heat of a spirit-lamp flame. Instead of reducing sulphuret of antimony by heating it in contact with black flux, it is even better to effect a similar result by transmitting hydrogen gas over it, as described at page 473.

(2) A solution containing antimony being added to the materials for liberating hydrogen gas (*i.e.* sulphuric acid, water, and zinc), antimoniuretted hydrogen gas is formed, which deposits a crust of metallic antimony when ignited, or when passed through a narrow glass tube heated by a spirit-lamp flame. In connxion with the generation of antimoniuretted, or with arseniuretted hydrogen, it is of especial importance to bear well in mind the fact that both zinc and sulphuric acid occasionally contain arsenic as a casual impurity. The absence of arsenic can be insured by liberating a portion of hydrogen from the zinc, sulphuric acid, and water, and igniting it as a jet previously to the addition of a supposed antimonial solution.

TELLURIUM.

Equivalent, or atomic weight . . .	64·2
Specific gravity	6·26

Notwithstanding the metallic aspect and considerable density of tellurium, its relations so nearly approach those of sulphur and selenium, that its claims to the metallic character are not fully admitted. It occurs, for the most part, in association with bismuth, gold, silver, or lead; occasionally, however, it has been found isolated. Tellurium may be most readily extracted from Hungarian sulpho-telluret of Bismuth, found near Chemnitz, by a process of which the following presents an outline:—Equal weights of the powdered ore and dry carbonate of soda are made into a paste with oil and exposed to a strong white heat in a covered crucible. By this operation metallic

bismuth is liberated, and sulphuret and telluret of sodium formed. The two latter constitute a fused mass, which being dissolved in water, and the solution exposed to the atmosphere, decomposition ensues: metallic tellurium is deposited, and caustic soda, mixed with hyposulphite of soda being formed by oxidation of the sulphur previously contained in the sulphuret of sodium.

Properties.—In colour tellurium assimilates itself to silver and to antimony. It is a brittle metal and a bad conductor of heat and electricity. It fuses by a heat slightly below redness, and at a higher temperature volatilizes. If atmospheric air be admitted whilst the tellurium is yet hot it burns, yielding tellurious acid. Two oxides of tellurium are known, tellurious acid $Te\,O_2$, and telluric acid $Te\,O_3$. They are produced from tellurium exactly as selenious and selenic acids are produced from selenium, to which, therefore, the student may refer. The remaining combinations of tellurium are unimportant.

ARSENIC, OR ARSENICUM.

Equivalent, or atomic weight . .	75
Specific gravity	about 5·8

Arsenic is rarely, though sometimes found uncombined in nature; but by far the largest amount is obtained by a process of sublimation from ores (arseniurets) containing it. Arseniurets of iron, nickel, and cobalt are the chief. When an arseniuret is heated in an atmospheric current, the metallic arsenic oxidises, becomes arsenious acid, sublimes, and condenses.

Preparation.—Metallic arsenic or arsenicum is obtained by incorporating arsenious acid, or white oxide of arsenic as it is sometimes called, with charcoal or black flux, and exposing the mixture to heat in a close vessel. Carbon uniting with oxygen forms carbonic oxide and acid, whilst metallic arsenic is reduced, and sublimes.

Properties.—Arsenic has a full metallic lustre, somewhat like steel in appearance. It is brittle and crystalline. When heated in vessels to which the atmosphere has free access, it readily oxidizes and becomes white oxide of arsenic, more properly called arsenious acid; but when heated in close vessels it sublimes before fusion, and covers the interior of the vessel with a mirror-like scale. The vapour of metallic arsenic has the odour of garlic, a characteristic of some importance in certain medico-legal investigations, though less valuable than formerly. About 150 years since, a German writer on Toxicology, Reisseissen, stated the smallest amount of arsenic he could discover in a dead body to be ten grains, and he recommended as a somewhat delicate means of ascertaining the presence of arsenic, to burn the corpse entire, and remark by occasional smelling whether it gave off an alliaceous odour. This was a somewhat rude expedient, nevertheless the alliaceous odour of vapourized arsenic is not an indication to be despised. The student may convince himself of the fact easily, as follows:—Wine and spirit bottles have occasionally green lables; strip off a portion of one of these lables, burn it, and remark the powerful alliaceous odour which is diffused: this depends upon the presence of the arsenical pigment called Scheele's green.

Arsenic with Oxygen.

Two compounds of arsenic with oxygen are known; both of them have acid properties, and combine with bases to form definite salts: they are arsenious acid AsO_3, and arsenic acid AsO_5.

Arsenious Acid—White Oxide of Arsenic, or White Arsenic.

This substance is of the highest importance, as being the frequent agent of criminal or accidental poisoning. Although the violence of arsenious acid, considered as a poison, is inferior to that of many others, there are few substances so much to be feared, being almost tasteless; it can be mixed with articles of food and swallowed without discovery, and there is no practically efficient antidote for staying its destructive agency.

Properties.—Arsenious acid occurs as a heavy white vitreous-looking substance, breaking with a conchoidal fracture. Some varities are almost transparent, others are opaque; the difference between the two not being referable to any variety in chemical composition, but merely to an allotropic cause. The opaque variety is slightly more soluble in water than the other, 100 parts of boiling water dissolving about 11½. Nearly three-fourths, however, of this amount separate as the water cools. Alkaline solutions readily dissolve arsenious acid, generating salts called arsenites. Hydrochloric and sulphuric acid also dissolve it; more especially the former: boiled with nitric acid it acquires more oxygen, and becomes arsenic acid $As\ O_5$. Arsenious acid can be readily sublimed, the heat of a spirit-lamp flame being amply sufficient for the purpose. Its vapour condenses and yields small but brilliant octahedral crystals, which are very characteristic. Solutions of arsenious acid yield no precipitate with nitrate of silver, except ammonia or some other alkali be present; nor must the alkali be in excess. But when the nitrate of silver and alkali are duly apportioned a yellow precipitate occurs, similar in appearance to phosphate of silver, for which it is occasionally mistaken. The mixture in proper proportions of nitrate of silver with ammonia, and called ammoniacal nitrate of silver, is a valuable test for indicating the presence of arsenious acid. Ammoniacal nitrate of silver is prepared by adding solution of ammonia to solution of nitrate of silver, until the oxide of silver thrown down is nearly dissolved, but not *quite*. Proceeding thus, the operator is assured that ammonia does not exist in excess. Arsenic acid, the next compound to be described, yields a precipitate with arsenic acid, even though no alkali be present, and the precipitate is brick-red.

Solution of sulphate of copper treated with solution of ammonia, as just described for nitrate of silver, forms what is called ammoniacal sulphate of copper, which is also a delicate test for arsenious acid, with which it throws down a green precipitate (Scheele's green).

Hydrosulphuric acid and hydrosulphates throw down a yellow precipitate.

The method of discovering the presence of arsenious acid in organic solutions, and separating it for judicial purposes, will be described presently; before doing so, it is desirable to discuss the characteristics of the other arsenical preparations.

Arsenic Acid—($As\ O_5$).

Preparation.—Arsenious acid is boiled with successive portions of nitrohydrochloric acid until nitrous acid fumes are no longer evolved; the solution being evaporated to dryness, yields anhydrous arsenic acid.

Properties.—Anhydrous arsenic acid is a white non-crystalline body, easily soluble in water, and yielding, on slow evaporation of the aqueous solution, crystals of hydrate of the acid. By strongly heating arsenic acid it suffers decomposition, oxygen gas and arsenious acid being evolved. It will be seen, by inspection of the formula $As\ O_5$, that

arsenic acid is analogous in composition to phosphoric acid. Like phosphoric acid also, it is tribasic, and it forms salts isomorphous with phosphates, thus establishing a more complete parallelism between the two. Three arseniates of soda are known, in two of which water counts for a portion of the three basic equivalents. The alkaline phosphates which contain basic water part with the latter when strongly heated; but, unlike the alkaline phosphates, they recover the basic water again by resolution in that liquid.

Arsenic acid in solution yields, with nitrate of silver, a brick-red precipitate, which is the arseniate of oxide of silver; it also yields a yellow sulphuret with hydrosulphuric acid and hydrosulphates. The sulphuret produced under these circumstances is similar in colour to that yielded under parallel conditions with arsenious acid and arsenites; but it differs in composition, and is not precipitated with equal facility.

Arseniates, or combinations of arsenic acid with bases, may be prepared directly by saturating the acid with base and evaporating; frequently, too, they admit of being prepared by deflagrating arsenious acid with the nitrate or chlorate of the base intended to enter into combination with arsenic acid,—the change is referable to the powerfully oxidising agency of nitric and chloric acids.

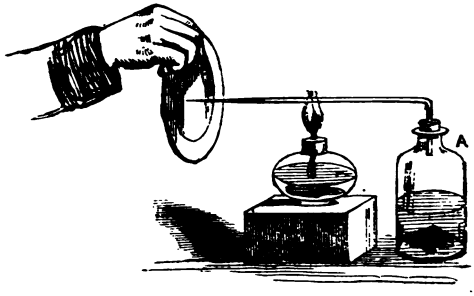
Arsenic with Hydrogen—Arseniurets of Hydrogen.

Two of these compounds are known, one is a gas the other a solid. Gaseous arseniuret of hydrogen—or *arseniuretted* hydrogen, as it is more frequently termed—is of especial interest in toxocological researches involving the extraction of arsenic.

Gaseous Arseniuret of Hydrogen, or Arseniuretted Hydrogen.

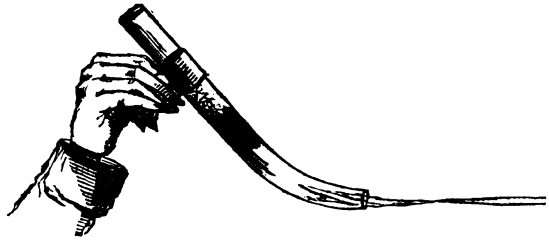
Preparation.—By generating hydrogen gas in contact with any arsenical solution, the gas in question is formed, mixed however with variable portions of hydrogen, of which I shall take no cognizance here, seeing that the presence of such does not affect the points in connexion with arseniuretted hydrogen, to which attention will be hereafter drawn.

The property which nascent hydrogen possesses of combining with arsenic and forming arseniuretted hydrogen, is of such great importance that the student should familiarize himself with it. For this purpose he cannot do better than employ the simple apparatus composed of a phial bottle of about six ounces capacity, having attached to it a perforated cork and tube bent at right angles and drawn out into a jet, as represented in the accompanying diagram:



The materials for generating hydrogen,—*viz.*, zinc and dilute sulphuric acid, being put into the bottle A, hydrogen will be evolved. Let the operator first assure himself that neither the zinc nor the sulphuric acid employed

contains arsenic; this he may do by igniting the gas as it escapes through the jet, and causing the tongue of flame to play against a piece of white porcelain,—a plate, for instance. If the gas burn without producing any stain the materials are free from arsenic. Let the operator now remove the cork, and drop into the bottle where hydrogen is still being developed, the minutest quantity of a solution of arsenious acid, and, having waited a few seconds, until all the atmospheric air contained in the bottle has been expelled, again ignite the jet of gas. It will now be found to burn in a very different manner. It will deposit a black mirror-like stain on the white porcelain; it will deposit a similar stain within the horizontal glass tube, corresponding with the portion heated by the spirit-lamp flame; and lastly, if burned in a tube open at both ends and held at an angle as in the annexed diagram, the interior of the tube will become coated with two layers, one of metallic arsenic, the other of arsenious acid.



Arseniuretted hydrogen thus employed, as a means of removing and discovering arsenic, is called *Marsh's test*, from its inventor, Mr. Marsh. There is no chemical impediment to its acting in organic solutions,—such as the contents of a stomach, for example; but a mechanical action sometimes interferes. Occasionally, with certain kinds of organic solutions, a bubbling or frothiness occurs, causing moisture to pass through the delivery tube, and extinguish the jet. A little oil mixed with the hydrogen-liberating arsenical solution, will sometimes remedy this defect; or occasionally a few filaments of asbestos: nevertheless, it will be generally advisable to separate a portion at least of the organic matter, by processes soon to be described, before having recourse to the arseniuretted hydrogen test.

The second, or solid, combination of arsenic with hydrogen, may be disposed of in few words: it is found in small quantity during the combustion of the preceding compound.

Sulphur with Arsenic—Sulphurets of Arsenic.

Of these compounds, several are known; but their individual consideration will be unnecessary. It will suffice to divide them into realgar, or the red sulphuret, and orpiment, or yellow sulphurets.

Realgar, $As\,S_2$, is found native, and it may also be formed artificially by heating a mixture in the necessary atomic proportions of arsenious or arsenic acids with sulphur. It is red, and like all other sulphurets of arsenic volatile, and, like them, yields up metallic arsenic when mixed with black flux, and heated in close vessels.

Orpiment (auri pigmentum) also occurs naturally, and may be prepared by fusing a mixture of arsenious acid and sulphur in due proportions, or by precipitating a solution of arsenious acid and by hydrosulphuric acid. Both these orpiments have the composition $As\,S_2$. The orpiment generated by transmitting hydrosulphuric acid through a solution of arsenic acid has the composition of $As\,S_5$, and, therefore is the sulphur correspondent of arsenic acid.

Chlorine with Arsenic—Chloride of Arsenic.

Only one compound of chlorine with arsenic is known. It is prepared by transmitting chlorine over arsenic as in the process of generating the chlorides of sulphur and of phosphorus. It may be also prepared by distilling a mixture of one part metallic arsenic and six of corrosive sublimate. Chloride of arsenic is a volatile colourless liquid, boiling at 269°Fah. and evolving a vapour, the density of which is 6·3.

In dealing with organic solutions containing arsenious acid and hydrochloric acid, it is necessary to bear in mind and provide against the volatility of chloride of arsenic, as we shall learn in the sequel.

Toxicological Examination for Arsenious Acid.

Toxicological chemistry is a department of itself: one elaborate and complex, involving special points of consideration which treatises on general chemistry do not usually take cognizance of. The subject of arsenious acid, however, regarded as a poison, is so important that an outline at least of its toxicological relations must be given.

The discovery of arsenious acid in colourless solutions, free from organic matter is a problem of sufficient ease: when, however, organic matters are present, especially when the latter are thick and coloured, the difficulties increase, and the utmost care and skill of the experimenter are required.

Toxicological knowledge to be valuable should be available. In all that relates to the administration of antidotes there is no time for consulting books,—the antidote to be useful should be given at once. Cases of poisoning by arsenious acid are chiefly those in which it has been administered by a second party; the instances in which it is taken as a suicidal agent are more rare. This is an important circumstance for remembrance. The time which elapses between the administration of arsenious acid and the manifestation of symptoms of poisoning, will vary according to the state of aggregation of the material. A case is on record of a person biting off small pieces of massive arsenious acid; the symptoms did not manifest themselves for some hours, whereas if the poison be swallowed in powder, or in partial solution, the effects are manifested more speedily—rarely, however, in less time than half an hour: this too is an important point to be remembered. It is astonishing how half digested knowledge fleets away in the terror and excitement attendant on poisoning. I once remember being called to visit an individual supposed to have been poisoned; she was a girl who, having determined to commit suicide, obstinately refused to supply any information. I found her supported by a medical man and his assistant, one on each side. They were walking her up and down the room with the intention of preventing sleep, the idea being that she had taken a poisonous dose of laudanum. The only reason for the impression, and a very illogical reason it was, consisted in the fact that the dress was stained with dark spots. Now laudanum is dark coloured, hence in the opinion of these concerned she had taken laudanum. But the patient was in agonies; her lips were parched and corroded, and the ejected matter, although it had blackened the white parts of her dress, had tinged a black handkerchief red. Apparently the poison which she had taken was oil of vitriol; and a tumbler found on the mantelpiece, still sour from lingering portions of the fatal draught completed the evidence. Half an hour had been lost by the disgraceful mistake, and each step the patient had been made to take was a step towards death. She died of course.

Treatment of a Case of Poisoning by Arsenious Acid.—Supposing the poisoning to have been clearly traced to arsenious acid, copious draughts of hydrated peroxide of

iron suspended in water should be at once given. This substance cannot be purchased; it must be prepared when wanted, by adding ammonia or its carbonate to tincture of chloride of iron, a liquid which may be procured at any druggists. Two or three quarts of the tincture may be taken, and ammonia, or carbonate of ammonia, in solution added until no further precipitation is occasioned. The precipitate is collected on a thin piece of texture, say a handkerchief well washed with boiling water to remove the alkali, and administered; meantime medical advice should be sought, and the stomach-pump employed, for even the hydrated oxide of iron is not an antidote to be relied upon. Arsenious acid is almost the only irritant poison in the treatment of cases of poisoning by which the stomach pump is eligible.

Detection of Arsenious Acid in Mixed Solutions.

(1) Let us assume that arsenious acid is supposed to exist in a stomach, the contents of which are milk, beer, bread, and meat: a mixture of greater complexity than this does not usually occur. The investigation should be conducted as follows:—Place the stomach on a clean glass or porcelain dish, cut it open with scissors, turn out the contents, and examine the mucous or internal coat of the stomach carefully by a lens. Any little white particles discovered by this scrutiny should be carefully removed, and their nature determined by one or more of the tests for arsenious acid already detailed. If the presence of arsenious acid be thus determined much trouble will be saved, and the operator will proceed with greater confidence.

(2) The mixed solution being thrown upon a cloth filter, or rather, a fine net, is to be roughly strained, the solid matter well washed with distilled water, separated, and put aside. Let us indicate this solid matter by A.

(3) The filtrate, or what has come through the filter, is now to be strongly acidulated with acetic acid, by which means a considerable portion of organic matter will be reduced to the solid condition. Straining will remove this solidified matter, which, being washed with hot water, is to be added to A.

(4) The filtrate is now to be evaporated over a lamp or on a sand bath to dryness, taking care that the heat applied be not sufficiently high to cause the evaporation and loss of any part of the arsenious acid. This avoidance of loss may be insured by thrusting several fine slips of paper quite through the material under process of drying, in such manner that one end of each slip of paper may come in contact with the dish. From time to time a slip is to be withdrawn; and immediately the lower end of one of these slips becomes somewhat dark, from incipient charring, the process of heating must cease. The dish and its contents being allowed to cool, hot water is added to effect the solution of arsenious acid, and the dried material is to be added to A. This process of solution and re-evaporation several times repeated will usually succeed in effecting the separation of enough organic matter to permit the application of tests.

(5) A portion of the filtrate or filtered liquor, now somewhat free from organic matter, is to be acidulated with hydrochloric acid, and boiled with slips of metallic copper. Probably a coating of arsenic will be deposited on the copper; if so, the whole of the filtrate may be treated separately, for there can be no better means of effecting the separation of arsenic out of solutions containing arsenious acid. Sometimes, however, the process will not succeed, on account of the presence of nitrates and some other bodies. This is called *Reinsch's test.* The copper slips with arsenical coating are to be collected, dried, placed in a test-tube, and the tube heated, when arsenic, quickly changing to arsenious acid, by further application of heat sublimes.

(6) If Reinsch's test does not succeed, dilute sulphuric acid and zinc are to be placed in the vessel depicted at page 478, or at page 473, and the absence of arsenic determined as stated at page 479; a portion of the filtrate is now to be added, and the remaining portion of the operation conducted as before mentioned (page 479). In order to guard against the inconvenience of frothing or bubbling, a pledget of cotton-wool or asbestos may be placed in the tube, which, in diagram page 473, contains dried chloride of calcium: chemically dry arseniuretted hydrogen gas is not required in our present experiment.

(7) The remaining portion of the filtrate may (though it is unnecessary if the preceding schemes of treatment succeed to have recourse to any other) be precipitated by hydrosulphuric acid, and the resulting sulphuret collected, and reduced by means of black flux and heat

It now remains to deal with the solid matters, A; and, before the processes to be followed are described, it will be necessary to remind the student that arsenious acid is converted into arsenic acid by boiling with nitric or nitro hydrochloric acid; in like manner arsenious acid, by ignition with nitrate or chlorate of potash, becomes arseniate of potash. These facts being remembered, the chemistry of the following treatment will be intelligible. Cut the solid matter into small pieces, and boil with solution of potash until all the animal matter is dissolved, or at least very much disintegrated; next add nitric acid in excess by gradual small proportions, and evaporate the whole to dryness. The dry material being removed and packed in a porcelain or platinum crucible, is to be incinerated until all carbonaceous matter is burned away. Arseniate of potash now remains, from which sulphuret of arsenic may be thrown down by a current of hydrosulphuric acid. The sulphuret being collected, mixed with black flux, and heated in a tube, yields metallic arsenic.

In this sketch of the process to be followed in effecting the separation of arsenic from organic bodies containing arsenious acid, no application has been made of what are known as *liquid tests*—namely, *ammoniacal nitrate of silver* and *ammoniacal sulphate of copper*. The fact is, that the tests in question are subject to many fallacies when applied to organic arsenical liquid; if, however, the operator have applied one or both of these tests, he should be aware that the precipitates yielded by them, *if arsenical*, yield a characteristic arsenical crust when mixed with black flux, and heated in a tube closed at one end.

Distinction between the Arsenical and the Antimoniacal Crust.—Sulphuret of antimony and sulphurets of arsenic, to which may be added arsenical solids *generally*, are both decomposed when mixed with black flux, and heated in a tube closed at one end, the metal arsenic or antimony being liberated in either case. Much is written concerning the probability of confounding the metals; but the mistake can only occur to a very careless operator. Metallic arsenic is easily volatilized by mere spirit-lamp heat, and can readily be chased from one end of a closed tube to the other, yielding a fresh crop of arsenious acid crystals by each fresh volatilization. Antimony does not admit of being thus easily volatilized, not even when the flame is intensified by means of the blowpipe. This simple characteristic suffices to distinguish the two metallic crusts.

Does Arsenic exist as a Normal Constituent of Animal Bodies?—Orfila at one time entertained the affirmative opinion, but he subsequently altered this opinion. From time to time the question has been since mooted, but I think we may take it for granted that the most skillfully devised and carefully executed chemical processes have failed to discover arsenic as a normal constituent of animal structures.

Change of Arsenious Acid into Sulphuret of Arsenic (orpiment) by Contact with Decomposing Animal Matters.—Sulphur being a constituent of animal matters, and hydrosulphuric acid being a result of their decomposition, it follows that a corpse interred with arsenious acid (white arsenic) in the stomach or intestines, allowed to remain buried some time, and subsequently exhumed, may not contain a trace of arsenious acid remaining, the whole of the latter having been converted into orpiment.

URANIUM.

Equivalent or atomic weight	60
Specific gravity	?

This is a rare metal. It is chiefly found in two minerals, *pitchblende* and *uranite*, from the first of which it is generally extracted in the condition of nitrate of sesquioxide of uranium by the following process:—Pitchblende having been reduced to fine powder, is treated with nitric acid, the solution evaporated to dryness, and re-dissolved by water. The solution is again evaporated to a convenient extent, and set aside to deposit crystals of nitrate mixed with sesquioxide of uranium. The mother liquor being decanted, is evaporated a second time, to cause a fresh deposition of crystals. But the mother liquor still contains nitrate of uranium, which refuses to crystallize on account of the large amount of extraneous bodies present, chiefly copper, lead, and arsenic. These metals are all precipitated by a current of hydrosulphuric acid gas, which *does not throw down uranium.* The liquor being now filtered and evaporated, yields a third and final crop of nitrate of uranium, still mixed with slight impurities, from which it is isolated by means of ether, which has the property of dissolving nitrate of uranium.

Development or Preparation of Uranium.—By acting on its chloride by potassium, similarly to the process employed for developing magnesium.

Uranium, with Oxygen Oxides of Uranium.—Two distinct oxides of uranium are known—the protoxide UO, and the sesquioxide U_2O_3.

Protoxide of Uranium.

Preparation.—(1) By transmitting a current of dry hydrogen gas over the oxalate of sesquioxide of uranium, heated to redness in a porcelain tube.

(2) As a hydrate, by adding solution of ammonia to protochloride of uranium.

Protoxide of uranium, when heated to redness, absorbs oxygen, and yields a black oxide, having the formula U_3O_4. It is to be regarded as a salt rather than a distinct oxide, and may be considered as a compound of protoxide and sesquioxide of uranium. Heated still more strongly, it becomes further changed into another compound oxide, represented by $2UO.U_2O_3$.

Sesquioxide of Uranium—(U_2O_3).

This oxide, which is the base of yellow uranium salts, has not yet been isolated; but the hydrate of sesquioxide of uranium $U_2O_3 + 2HO$ is formed by exposing a solution of oxalate of uranium to solar light, collecting the brown matter produced on a filter, and exposing it freely to atmospheric air. Hydrated sesquioxide of uranium is a yellow powder.

Salts of the Oxides of Uranium.

There are not many salts of the protoxide of uranium, and those which exist are unimportant. Their solutions are characterized by a green tint. The sesquioxide of uranium forms a large number of readily crystallizable salts, having an atomic constitution different from all other known salts of a sesquioxide. Salts of sesquioxide of uranium furnish the only exception to the rule, that the number of atoms of nitric acid in a nitrate is five times the number of atoms of oxygen in the base, and the number of atoms of sulphuric acid in a sulphate is three times the number of atoms of oxygen in the base. Now the nitrate of sesquioxide of uranium, even when crystallized from a solution holding a large excess of acid, has the formula of $U_2O_3\ SO_3$; whereas, to be accordant with other sulphates of sesquioxides, it should have the composition of $U_2O_3\ 3SO_3$. Again, the nitrate of sesquioxide of uranium, even when crystallized out of a solution containing a large excess of acid, has the composition $U_2O_3\ NO_5$. With the view of explaining this anomaly, some chemists regard sesquioxide of uranium as really the protoxide of a radical termed *uranile*, which latter has the composition of protoxide of uranium reduplicated, and consequently would be expressed as (2UO). According to this theory, sesquioxide of uranium, or *protoxide of uranile*, would be expressed by (2UO)O, when the nitrate of sesquioxide of uranium would be indicated by $(2UO)O\ NO_5$, and the sulphate of sesquioxide of uranium by $(2UO)O\ SO_3$.

A yellow colour is the general characteristic of all the solutions containing sesquioxide of uranium, or protoxide of uranile. Alkalies throw down from these solutions a yellow precipitate compound of the oxide (acting as an acid) with the alkali. Carbonates of alkalies also throw down a yellowish precipitate, which is a double carbonate of the alkali with sesquioxide of uranium. All the green or protosalts of uranium may be converted into the yellow or sesquisalts by boiling with nitric acid.

The black or compound oxide of uranium is employed in the arts of glass-staining and porcelain-painting to impart a black colour; the sesquioxide is used in the same arts for imparting a yellow colour.

General Characteristics of Sesquisalts of Uranium.

A solution assumed to contain uranium should be boiled with nitric acid, for the purpose of raising the metal to the condition of sesquioxide, when the following tests will indicate the presence of uranium :—

Solutions of potash and soda throw down a yellow precipitate.

Ferrocyanide of potassium yields a mahogany-coloured precipitate.

Hydrosulphate of ammonia throws down a dark-brown precipitate, but hydrosulphuric acid none.

TUNGSTEN, SCHEELIUM, OR WOLFRAMIUM.

Equivalent or atomic weight	95
Specific gravity	17·5

Preparation.—(1) By transmitting a current of hydrogen gas over tungstic acid, heated to redness in a porcelain tube.

(2) By heating tungstic acid mixed with charcoal powder and oil, in a crucible lined with charcoal.

Properties.—A lustrous metal of difficult fusibility, not oxidising by exposure to the

air at ordinary temperature, but absorbing oxygen at a red heat, being converted into tungstic acid. Nitric acid attacks tungsten violently even whilst cold, changing it into tungstic acid; and a similar change is effected by hot sulphuric acid.

Combinations of Tungsten with Oxygen—Binoxide of Tungsten—(WO_2).

Preparation.—(1) By transmitting a current of hydrogen over tungstic acid, heated not above dull redness, in a tube of porcelain.

(2) Mix intimately two parts of powdered wolfram (native double tungstate of iron and manganese) with four parts of carbonate of potash, and fuse the mixture in a platinum crucible. Act on the fused mass by water and filter. The filtrate contains tungstate of potash; it is to be evaporated to dryness, with one part of sal-ammoniac, the residue calcined at a red heat, and lixiviated with water, when the binoxide of tungsten will remain in the form of a black powder.

Properties.—The binoxide of tungsten is a black powder, readily absorbing oxygen, and changing to tungstic acid when heated in the presence of atmospheric air; it also generates tungstic acid when boiled with a strong solution of caustic potash.

Tungstic Acid—(WO_3).

Preparation.—We have already seen that metallic tungsten, or binoxide of the metal, generates tungstic acid when strongly heated in presence of atmospheric air; it may be also readily prepared by acting upon tungstate of lime with hot nitric acid, which removes the lime and leaves the tungstic acid.

Properties.—A yellow powder, insoluble in water and in acids, but soluble in ammoniacal and fixed alkaline solutions, provided it has not been calcined.

The sulphurets and chlorides of tungsten are not important.

MOLYBDENUM.

Equivalent or atomic weight . . .	46
Specific gravity	8·6

Preparation.—(1) By transmitting a current of hydrogen gas over either of the oxygen compounds of molybdenum contained in a porcelain tube, and heated to redness.

(2) By mixing either of the oxygen compounds of molybdenum with charcoal powder and oil, and heating the mixture strongly in a crucible lined with charcoal.

Properties.—A brittle white metal of great infusibility, and changing by absorption of oxygen, when heated in atmospheric air, into molybdic acid.

Compounds of Molybdenum with Oxygen.

Three oxygen compounds of molybdenum are known,—the protoxide, the binoxide, and molybdic acid.

Protoxide of Molybdenum—(MO).

Preparation.—Hydrochloric acid is poured into a solution of molybdate of potash, soda, or ammonia, until all the molybdic acid first thrown down is redissolved. A sheet of zinc now being immersed in the liquor speedily colours it black, owing to the generation in it of chloride of zinc and protochloride of molybdenum. Ammonia is now to be dropped in until the liquid becomes colourless, and all the molybdenum has been thrown down in the condition of protoxide. The latter must be collected, rapidly washed and dried without atmospheric contact.

Binoxide of Molybdenum—(MO_2).

Preparation.—(1) By the application of heat to molybdate of ammonia contained in a closed vessel.

(2) By calcining a mixture of molybdate of soda and sal-ammoniac.

Properties.—Binoxide of molybdenum is a reddish-brown crystalline powder, which unites with water and generates a hydrate, something like hydrate of peroxide of iron.

Molybdic Acid.

This is the most important of all the oxygen compounds of molybdenum; and from it, as we have seen, the other oxygen compounds of the metal are generated.

Preparation.—It has been stated that when metallic molybdenum is strongly heated in the presence of atmospheric air it becomes converted into molybdic acid; practically however, the preparation of molybdic acid is anterior to that of molybdenum, and is conducted as follows:—Native bisulphuret of molybdenum, $Mo\,S_2$, is digested with hot nitrohydrochloric acid, by which treatment the sulphur of the mineral is converted into sulphuric acid, and the molybdenum into molybdic acid. The whole is evaporated to dryness, and the residue being digested with ammonia, molybdate of ammonia is formed, and may be obtained in crystals by evaporation. By strongly heating molybdate of ammonia in the presence of atmospheric air, decomposition ensues, ammonia is evolved, and molybdic acid remains.

Properties.—A white powder, which may be volatilized at a strong red heat, but with difficulty. When recently precipitated from solutions containing it, molybdic acid is slightly soluble in water, but completely insoluble in that liquid, after having been calcined. It is more soluble in acids, nevertheless it does not act as the basic constituent of any well-defined and permanent salts.

VANADIUM.

Equivalent or atomic weight	68·6
Specific gravity	uncertain

Vanadium is a rare metal, which occurs in combination with iron in certain parts of Sweden, and also associated with lead, as vanadiate of the oxide of that metal.

Preparation of Vanadium.—(1) By heating vanadic acid with potassium in a platinum crucible, and acting on the residue with water, by which treatment potash is dissolved out, and vanadium remains.

(1) By transmitting ammoniacal gas over chloride of vanadium heated to redness in a glass tube.

Properties.—A white, brittle, lustrous metal, highly infusible, and very unchangeable, not being acted upon by air, water, sulphuric, nitric, or hydrofluoric acid; nitrohydrochloric acid dissolves it however, generating a blue solution.

Compounds of Vanadium with Oxygen.

Three of these compounds are known—Protoxide of vanadium, VO; binoxide of vanadium, VO_2; and vanadic acid, VO_3.

Protoxide of Vanadium.

Preparation.—By heating vanadic acid in a current of hydrogen gas.

Binoxide of Vanadium.

Preparation.—(1) By mixing ten parts protoxide of vanadium with twelve of vanadic acid, and heating the mixture in a vessel holding carbonic acid gas.

(2) Thrown down as a hydrate by the addition of carbonate of soda to any salt containing the binoxide as base.

Properties.—The anhydrous binoxide is a black powder, which, if exposed to the atmosphere, and especially if heated, absorbs oxygen, and becomes vanadic acid. The hydrated binoxide is a grayish-white powder, changing to brown by exposure to the air, from absorption of oxygen.

Vanadic Acid.

Preparation.—By dissolving native vanadiate of lead in nitric acid, the former is decomposed, nitrate of lead being generated, and vanadic acid set free. Water being now added a solution of nitrate of lead results, and vanadic acid being insoluble remains; being impure, however, it is taken up by ammonia in the form of vanadiate of ammonia, crystallized by evaporation, and finally the vanadiate of ammonia decomposed by heat, when ammonia is expelled and pure vanadic acid remains.

Properties.—A deep orange-coloured or brown powder, almost insoluble in water, more soluble in acids (although it does not yield definite salts with them), but readily combines with bases forming *vanadiates*, of which those containing an alkaline base are soluble in water. Vanadic acid is a powerfully oxidising agent, readily imparting oxygen to bodies characterized by a strong tendency to appropriate that element—such as sulphurous acid, sugar, alcohol, &c.

Vanadium with Chlorine—Chlorides of Vanadium.

Two chlorides of vanadium are known, the bichloride and the terchloride. The former is prepared by dissolving vanadic acid in hydrochloric acid, transmitting a current of hydrosulphuric acid gas through the solution, and evaporating to dryness. The terchloride of vanadium results when a current of dried chlorine is transmitted over a mixture of vanadic acid and charcoal. Bichloride of vanadium is a brown powder; terchloride of vanadium a yellow volatile liquid.

COPPER.

Atomic or equivalent weight . . .	31·7
Specific gravity	8·76 to 8·96

This very important and anciently known metal occurs in many parts of the world, though Russia, Sweden, and the island of Cuba yield it in greatest purity. Native copper is not unfrequent, but the metal more frequently occurs in combination with oxygen, sulphur, and arsenic; carbonate of copper also exists, though it is more rare. About half the total amount of copper annually manufactured is produced in South Wales, from copper ores brought from Cornwall, Australia, New Zealand, and many other localities. South Wales became the head quarters of copper smelting on account of the immense coal fields of that district. The practice of Welsh copper smelting is complex and ingenious; the principle which it involves is, however simple, and may be rendered intelligible by the general statement, that whilst iron, one of the impurities associated with the greater number of copper ores, has a tendency to unite with oxygen when strongly heated, copper unites under similar circumstances with sulphur. This

mixed product being heated in contact with siliceous matter, silicate of oxide of iron forms, melts, and rises to the surface, whilst sulphuret of copper still undecomposed sinks below. When the iron slag (silicate of oxide of iron) has been removed, the furnace heat is raised sufficiently to effect the decomposition of sulphuret of copper into sulphurous acid, which escapes, and metallic copper, slightly contaminated with oxide of copper, remains. The metal holding this small portion of oxide is deficient in malleability, hence the oxygen of the oxide must be removed; this is accomplished by the process of copper-refining, as it is termed. The rough material being liquified by fusion, powdered charcoal is added, and the whole stirred by a green wooden pole. It is almost unnecessary to remark, that the pole thus circumstanced burns, evolving hydrogenous matters, and yielding carbon, both of which are strongly attractive of oxygen, the removal of which is consequently effected.

Preparation of Copper Chemically Pure.—By transmitting a current of hydrogen gas over black oxide of copper heated to redness in a tube of refractory glass or of porcelain.

Properties.—The physical properties of copper are familiar to most persons. Its colour (red) is peculiar. It is soft, malleable, and ductile, fusible at a strong red heat, and volatilizes, when heated to whiteness; the vapour burning with a characteristic green flame. Copper being frequently employed for the manufacture of culinary vessels, the changes which it undergoes when exposed to common chemical agents demand attentive study. Perfectly dry air does not tarnish copper, but exposed to moist air, a greenish deposit of carbonate, and oxide of copper results, to which the general term verdigris is sometimes applied, though in the rigid language of chemistry it should be restricted to indicate *acetate of oxide of copper*. Acid and ammoniacal fumes rapidly act on copper surfaces, generating crusts of varying composition, but participating in the characteristic of being extremely poisonous. Oils also act upon copper surfaces, and what is remarkable, the action is more vigorous at low than at high temperatures; hence, food prepared in copper vessels should never be allowed to grow cold in them. The best antidote to poisoning by copper is white of egg, beat up with water, and copiously administered, followed by an emetic—a dessert-spoonful of mustard mixed with a quart of warm water, and freely swallowed, is efficient.

Combinations of Copper with Oxygen—Oxides of Copper.

There are four compounds of copper with oxygen—the suboxide, protoxide, binoxide, and cupric acid.

Suboxide of Copper—(Cu_2O).

This oxide occurs native, both crystallized and amorphous; it may also be prepared artificially by the following processes:—

(1) By heating in a crucible a mixture of protoxide and metallic copper.

(2) By heating in a crucible a mixture of chloride of copper and carbonate of soda, and acting upon the fused result by water, which dissolves out chloride of sodium and carbonate of soda, leaving suboxide of copper.

(3) By boiling a solution of any protosalt of copper with sugar and solution of potash, when the suboxide precipitates.

(4) As a hydrate, having the composition of $4Cu_2O + HO$, by adding solution of potash to solution of protochloride of copper.

Properties.—This oxide of copper imparts a fine red tint to white vitreous matter, for which purpose it is employed. In the hydrated condition it dissolves in ammonia, without imparting to the latter a blue tint, by which characteristic it may be distinguished from the hydrate of the protoxide of copper, next to be described. The ammoniacal solution, however, if exposed to the air, absorbs oxygen, protoxide is formed, and the colour of the solution changes to blue.

Protoxide of Copper—(CuO).

Preparation.—(1) By heating metallic copper exposed to the air.

(2) By strongly igniting nitrate of copper.

(3) As a pale green hydrate, by adding potash, soda, or ammonia to any solution holding protoxide of copper. This hydrate, if boiled in the solution from which it has been precipitated, or if collected and heated, loses its water of hydration, and is converted into the anhydrous protoxide.

Properties.—The protoxide of copper is a black powder, somewhat hygrometric, and which readily yields up its oxygen when heated in close vessels along with carbon, hydrogen, and some other bodies which have the tendency to unite with oxygen; a property taken advantage of in the ultimate analysis of organic bodies. It combines with acids, and forms well-defined salts, mostly crystalline, and blue or green. Hydrated protoxide of copper dissolves in ammonia, with the generation of a blue solution, which is very characteristic.

Binoxide, sometimes called *deutoxide* of copper (CuO_2), is a compound of no practical importance, formed by acting on the hydrate of protoxide of copper by binoxide of hydrogen. It is a yellowish-brown powder.

Cupric Acid.

The atomic constitution of this compound is unknown. Cuprate of potash is prepared by heating a mixture of finely divided copper, potash, and nitre, and acting on the solution by water; cupric acid, however, has not been isolated.

Cupreous Salts.

Suboxide and protoxide of copper are basic, uniting with acids, and forming well-defined salts; binoxide of copper is neither acid nor basic, and cupric acid is devoid of all basic properties. All the most common and important salts of copper are salts of the protoxide.

Sulphate of Copper.

This important salt of protoxide of copper, known by the popular name *blue vitriol*, may be found by acting upon metallic copper with sulphuric acid. It is very largely employed in many arts and manufactures, especially for the purpose of volta-electric deposition, or the electrotype operation, as it is called. Sulphate of copper is soluble in four parts of cold, and half that weight of boiling water. Crystals of sulphate of copper belong to the doubly oblique system of Weiss and Mohs, and contain five equivalents of water. Four of the equivalents of water of hydration may be evolved by heat, but the fifth lingers with great obstinacy.

Nitrate of Copper.

A salt frequently employed in the laboratory, is made by dissolving metallic copper in nitric acid, and crystallizing the solution. When heated, it first changes into a

subnitrate, having the composition of $4CuO \cdot NO_5$; but if the heat be increased, the elements of nitric acid are completely evolved, anhydrous protoxide of copper remaining.

Carbonates.

No carbonate of copper having the composition of one equivalent of carbonic acid united with one atom of protoxide of copper is known. The precipitate which falls when solution of carbonated alkali is added to solution of protosalt of copper, has the composition $2CuO \cdot CO_2 + HO$. Two hydrocarbonates of copper occur native: one, *malachite*, is so extensively found in Siberia, that it is worked as a copper ore, and is employed instead of marble for ornamental tables, brooches, &c., occasionally, too, for door panels. *Malachite* has a composition represented by the formula $CuO.CO_2 + CuO.HO$; a second hydrocarbonate of copper, having the composition $2CuO.CO_2 + CuO.HO$ is found crystallized in the neighbourhood of Lyons; and when finely levigated is used as a pigment. A compound of the same kind, but still more pure, is made artificially, for employment as a pigment.

Acetates of Copper.

There are several compounds of acetic acid with protoxide of copper. The neutral acetate may be prepared by dissolving protoxide of copper in acetic acid, and evaporating the solution, when crystals form, holding either one or five equivalents of water according to the temperature at which crystallization is effected. Neutral acetate of copper is known popularly by the absurd term *distilled verdigris*. Many sub-acetates of copper are known under the generic term verdigris, and are generated by numerous processes.

In certain parts of France sub-acetate of copper is formed by moistening leaves of metallic copper with impure acetic acid, or stratifying them with the husks of grapes, from which the juice has been extracted. The operation is conducted in a pit dug in the earth, and the stratified copper leaves, after remaining for a period of two or three months, are taken out, moistened, and freely exposed to the atmosphere for the purpose of becoming oxidised. The final result is the formation of a crust of sub-acetate of copper, which may be removed by scraping; and the copper leaves, by further restratification, may be entirely converted into sub-carbonate. The sub-acetate thus produced is said by Regnault to have the composition indicated by the formula $CuO. C_4H_3O_3 + CuO. HO + 5HO$. Water decomposes this subacetate into a subsalt, having the following composition, $3CuO. C_4H_3O_3$, which deposits, and a solution containing two other acetates, having the respective composition of $CuO. C_4H_3O_3$ (neutral acetate), and a basic sub-acetate having the composition of $3CuO. 2C_4H_3O_3$.

Arsenite of Copper (Scheele's Green).

Under the head of arsenious acid, this substance has been mentioned as occurring when ammoniacal sulphate of copper is added to solution of arsenious acid. Potash or soda may take the place of ammonia, as far as the production of Scheele's green as a pigment is concerned, although ammonia is the alkali which should be had recourse to when a copper salt is used as a test for arsenious acid. On the large scale, Scheele's green is manufactured by dissolving arsenious acid in solution of carbonate of potash, and adding a solution of sulphate of copper. The tint of Scheele's green may be varied by varying the relative amount of ingredients used in making it.

Copper with Sulphur, Sulphurets or Sulphides of Copper.

Two of these compounds are known, one corresponding with the sub or di-oxide of copper, and which therefore has the composition of Cu_2S; the other corresponding with the protoxide of copper, and being represented by the formula CuS.

Disulphuret of Copper.

Preparation.—When copper filings or turnings are strongly heated in contact with sulphur, the two unite with brilliant combustion, yielding, as the result, the compound C_2S. This sulphuret is found native, and crystallized.

Protosulphuret of Copper.

Preparation.—By transmitting a current of hydrosulphuric acid gas, or adding a solution of hydrosulphuric acid or hydrosulphate of an alkali to a solution of salt of copper, a black powder falls: this is the hydrated protosulphuret of copper, which cannot be prepared by the dry way, nor when generated by precipitation is it permanent in the air. The application of heat drives off one equivalent of its sulphur and converts it into the *disulphuret.* A combination of this disulphuret Cu_2S with sulphuret of iron, Fe_2S_3, is a very widely distributed copper mineral, the well known *copper pyrites*, from which by far the major portion of copper is extracted.

Copper with Hydrogen (Hydruret of Copper). Copper with Nitrogen (Nitruret of Copper).

Both these compounds are known to exist and may be prepared artificially, but they are of small importance, and need not be further commented upon.

Copper with Chlorine—Chlorides of Copper.

Two combinations of chlorine with copper are known: the first being represented by the formula Cu Cl, and corresponding, therefore, with the sub or dinoxide of copper; the other having the composition of Cu Cl, and corresponding, therefore, with the protoxide. It will be convenient to give priority to the protochloride.

Protochloride of Copper.

Preparation.—(1) By dissolving metallic copper in nitro-hydrochloric acid, evaporating, and setting aside to crystallize.

(2) By dissolving oxide of copper in hydrochloric acid, evaporating the solution, and setting aside to crystallize. The crystals thus generated contain two equivalents of water.

(3) Anhydrous protochloride of copper is generated by heating copper in an excess of chlorine.

Properties.—A green compound, soluble in both water and alcohol, to which latter it imparts the property of burning with a green flame.

Sub- or Di-chloride of Copper.

Preparation.—(1) By boiling a mixture of copper filings with protochloride of copper.

(2) By exposing protochloride of copper to heat, when one atom of its chlorine is evolved, and di-chloride of copper produced.

(3) By adding solution of protochloride of tin to solution of protochloride of copper,

an excess of hydrochloric acid being present to guard against precipitation of oxide of tin.

Properties. A solid body, not very soluble in water, more readily soluble in hydrochloric acid, and with still greater facility in solution of ammonia. It fuses at about 750° Fah., and is totally volatilized at a red heat. Exposed to the air it rapidly decomposes, generating a compound of protoxide and protochloride of copper. A solution of di-chloride of copper in liquor-ammoniæ is sometimes employed for the purpose of abstracting oxygen from atmospheric air or other gaseous mixtures.

General Characteristics of Copper in Solution.—We may confine our attention to the *protosalts* of copper, inasmuch as these alone will occur in the course of ordinary investigation:—

(1) Ferrocyanide of potassium affords a mahogany-brown precipitate, which is very characteristic, inasmuch as the solutions of four metals only develope an appearance which is similar; they are copper, uranium, titanium, and molybdenum.

(2) Solutions of potash and of soda throw down a pale blue hydrate, which on boiling assumes a blackish hue.

(3) Solution of ammonia also precipitates the hydrated oxide, soluble in excess of ammonia, generating a solution with a purplish-blue tint. The evidence of this or the preceding test, taken in conjunction with No. 1, leaves no doubt as to the presence of copper.

(4) Solutions of carbonates of the fixed alkalies yield a pale blue precipitate, insoluble in excess of precipitant.

(5) Hydrosulphuric acid and hydrosulphuret of ammonia throw down a black sulphuret of copper.

ALLOYS OF COPPER.

The alloys of copper with other metals are numerous and important. Many of them were known and manufactured long before iron and steel came into use, not only serving for purposes to which copper alloys still continue to be applied, but many others to which they are less adapted. For example, cutting instruments were anciently made of copper alloys—varieties of bronzes. The late Sir Francis Chantrey devoted great attention to the subject of cutting bronzes; and in order to prove how well adapted a bronze might be made to the cutlers' uses, he caused a bronze razor to be fashioned, and shaved with it during many years. Modern brass, pinchbeck, and tombec, are alloys of copper with zinc. Brass of the ancients contained no zinc, but was an alloy of copper and tin. We should term an alloy of this kind *bronze.* Gun-metal is an alloy of eleven parts tin and one hundred of copper; bell-metal contains about twice that quantity of tin; and gong-metal somewhat less. The metal for telescope mirrors contains about thirty-three per cent. of tin, and statue bronze contains only about two per cent. of tin, melted with ninety-one per cent. of copper, six per cent. of zinc, and one per cent. of lead. Under the head of tin alloy of copper must here be noticed tinned copper surfaces. The operation of sheathing the surfaces of copper vessels to be employed in culinary operations with a tinned coating is one of great importance, and easily conducted. The copper to be tinned is heated over burning charcoal, smeared with sal-ammoniac, and tin rubbed upon it by means of tow, hemp, or a cloth. The tin adheres easily, completely sheathing the copper, and totally preventing, while it lasts, the occurrence of cupreous impregnation. Care, however, should be taken to discover the first appearance of tin abrasion, inasmuch as the copper

surfaces from which patches of tin have been removed are more soluble than if no tin were in their vicinity, on account of the voltaic action set up between the two metals in presence of a liquid solvent for copper.

MERCURY, OR QUICKSILVER.

Equivalent or atomic weight	100
Specific gravity	13·596

This metal is remarkable in being the only one which melts at a temperature lower than any naturally occurring, except nearly in polar latitudes; hence the inhabitants of temperate climes never meet with it in any other condition but that of liquidity, except artificial means have been adopted. Mercury can be frozen in any state of the atmosphere by certain freezing mixtures known to the chemist, amongst which, perhaps, a mixture of finely broken ice and crystallized chloride of calcium is most convenient. A mixture, however, of solidified carbonic acid with sulphuric ether is more rapid in its action. The freezing, and, consequently, the melting, point of mercury, for they are necessarily identical, corresponds with about the fortieth degree below zero of Fahrenheit's scale, or — 40° Fah.

The physical relations of mercury are of especial value to be studied by the chemist, inasmuch as this metal enters into the formation of two of his most useful instruments—the barometer and the thermometer. The exact amount to which a given volume of mercury expands for given degrees of temperature, is of the highest importance, as I have had occasion to mention in an early part of this treatise, when describing the mercurial thermometer, to which part the student may now turn with advantage.

Mercury boils somewhere about 660° Fah., and then becomes totally converted into vapour; but a portion of mercury is vaporized at ordinary temperatures, even under the usual atmospheric pressure of about 15 lb. avoirdupois to every square inch of surface. In vacuo the evaporation of mercury at ordinary temperatures ensues with still greater rapidity. Mercury, as found in commerce, is seldom pure, and as absolute purity is indispensable for mercury designed for barometric and thermometric uses, also for many other purposes, numerous means of purification have been devised. Considering the great volatility of mercury in comparison with other metals, the process of distillation would seem to be that most obviously indicated. Distillation indeed, is frequently had recourse to, and it serves to effect the separation of a large amount of impurities. The last traces, however, cannot be separated by this means, because many substances are volatilized when heated in contact with others of easy volatility, although they cannot be volatilized when alone at the temperature in question. This remark applies to the distillation of impure mercury.

Mercury may be completely purified by pouring upon its surface, and allowing to remain for some days, a mixture of one volume of aquafortis and two of water; this liquid dissolves the impurities, but not the mercury. The makers of thermometers and barometers effect the purification of their quicksilver by this means.

When small quantities of mercury have to be purified, that result may be accomplished by the following mixed process. First take some filtering paper, fold it into a conical shape, then cut off the apex of the cone so as to leave a very small orifice. By pouring mercury into the cone and allowing it to flow through the aperture, many of the superficial impurities will be filtered away and remain adherent to the sides of the

cone. The mercury, thus partially purified, is to be poured into a bottle of large comparative capacity and strongly agitated, the stopper being removed from time to time, for the purpose of admitting a fresh supply of air. By this treatment the metallic impurities contained in quicksilver are oxidised, whilst the mercury itself remains unacted upon. A peculiar rattling sound indicates when the operation of shaking has been continued sufficiently long. When nothing more remains to be oxidised, the mercury should be poured, as before, through the paper cone. Mercury, holding but a slight portion of any impurity, dissolved, loses its property of cohering into globular drops when poured upon a flat surface, and assumes the peculiar appearance designated by the expressive term *tailing*, that is to say each mercurial aggregation is not a globule but an irregularly elongated bar or tail.

Mercury is a somewhat rare metal, the localities yielding it being comparatively few. In Europe, the Spanish mines of Almaden in La Mancha, and the mines of Idria are ancient and celebrated. For a long period they continued to supply the total amount of mercury employed in the civilized world; but the quicksilver mines of Mexico and California have now sprung into importance. Native mercury sometimes occurs, though rarely; the greater amount of mercury is reduced from native sulphuret of the metal (cinnabar).

Mercury is not oxidised, or otherwise altered, by exposure to the atmosphere at ordinary temperatures; but if heated to something about its boiling point for a long time together—weeks, or even more—it gradually absorbs oxygen, and is raised to its highest grade of oxygenation. This oxide, when exposed to a still higher degree of heat evolves the whole of its oxygen, and is, therefore, occasionally employed as a source from which to obtain oxygen gas. Neither hydrochloric nor sulphuric acids, when diluted, exercise a perceptible solvent effect on mercury; mixed with strong oil of vitriol and boiled the acid is decomposed, sulphurous acid being evolved, and sulphate of oxide of mercury remaining.

Combinations of Mercury with Oxygen—Oxides of Mercury.

Two oxides of mercury are known,—one black, the other red; concerning the percentage composition of these oxides there is no uncertainty, but their atomic constitution is still open to some doubt, certain chemists regarding the black oxide as the sub, or dioxide, and the red oxide as the protoxide of mercury: whilst others recognize the former to be the real protoxide, and consider the red compound as a true peroxide of mercury. This doubtfulness is much to be regretted, inasmuch as it has produced a confusion of terms between two important medicinal agents,—calomel and corrosive sublimate. Now calomel is *quasi* harmless, but corrosive sublimate is a terrible poison; hence, any circumstance tending to the confusion of terms indicating these bodies is of grave importance. The same train of reasoning which leads to doubts as between the respective claims of black and red oxide of mercury to the appellation of *proto* or *peroxide*, also applies to the two chlorides. Hence calomel, formerly called the sub-chloride of mercury, afterwards the proto-chloride, becomes the sub- or di-chloride,—if the black oxide of mercury be recognized as the di- or sub-oxide, and corrosive sublimate, formerly called the oxymuriate of mercury, then the bi-chloride of mercury becomes the CHLORIDE OF MERCURY! the very name by which calomel is generally known at the present time. This instance goes far to demonstrate the general impropriety of designating chemical compounds, used medicinally, by names indicative of their composition; as between the expressions "*calomel*" and "*corrosive*

sublimate" there can be no mistake; but the chemical expressions indicative of these bodies are subject to change, according to a prevailing theory. For chemical reasons, much too long and numerous for indication here, I am disposed to treat of the black oxide of mercury as the sub-oxide Hg_2O, and the red oxide as the protoxide HgO.

Black Oxide (Suboxide or Dinoxide) of Mercury.

Preparation.—(1) By adding solution of potash or of soda to solution of neutral subnitrate of mercury. (2) By adding solution of caustic potash, or soda, or lime, baryta, or strontia water to calomel. Lime-water and calomel constitute the lotion known in medical and surgical practice, as the *black wash.*

Properties.—A dark brown, almost black, powder, which slowly decomposes when exposed to light, yielding metallic mercury and the red oxide of that metal.

Salts containing Sub-oxide of Mercury.

This oxide combines with most acids, giving rise to well defined salts. Sulphate of sub-oxide of mercury is generated by heating concentrated oil of vitriol with the metal in excess, or adding oil of vitriol to the sub-nitrate. Nitrate of sub-oxide of mercury is formed when cold by adding dilute nitric acid to metallic mercury, the acid being in excess. The composition of this salt is $Hg_2O\ NO_5 + 2HO$. If the mercury be in excess, a finely crystalline basic nitrate deposits, having the composition $3Hg_2O\ 2NO_5 + 3HO$. Both these salts are decomposed by the addition of water, a yellow subnitrate being in either case thrown down; indeed, a leading characteristic of the salts of sub-oxide of mercury, and many of the salts of protoxide of mercury, is their easy decomposition on the addition of water.

Red Oxide (Protoxide) of Mercury.

Preparation.—(1) By heating mercury for many weeks consecutively in a flask provided with a long neck, to a degree somewhat under the boiling point of the metal. The product of this operation is deep red and crystalline, and constitutes the *red precipitate* of the older chemists. Formerly when many chemical operations and forms of apparatus were designated by fanciful names, the long-necked flask employed in this operation was called *Boyle's Hell.*

(2) By cautiously heating any of the nitrates of mercury until the last traces of nitric acid, or its elements, are expelled. If a nitrate of a sub-oxide be the material employed, the sub-oxide absorbs the necessary amount of oxygen to raise it to the condition of protoxide. The product of this decomposition is paler than that generated by process No. 1, and its tint is not so fine. Traces of nitric acid, moreover, usually remain.

(3) By the addition of solution of potash, soda, lime, baryta, or strontia (lime, baryta, or strontia water), to a solution of chloride of mercury (corrosive sublimate). The oxide resulting from this treatment is red, but not crystalline like the preceding. If lime-water be employed in generating it, the result constitutes what is termed yellow wash in medical and surgical practice.

Properties.—All the leading qualities, physical and chemical, of this oxide, have been already described. Its colour (red) and its property of separating into metallic mercury and oxygen when heated, are amongst the most remarkable. Red oxide of mercury can assume two allotropic or isomeric states, distinguishable in the course of certain chemical operations. The red oxide generated by the moist process, or, in other words, by precipitation, combines with cold solution of oxalic acid, which

exerts no action upon the other varieties; it is besides more easily attacked by chlorine than they are.

Salts of Protoxide of Mercury. Nitrates of Mercury.

Preparation.—When mercury is boiled with excess of nitric acid, solution of neutral nitrate of protoxide of mercury (protonitrate of mercury) results. If this solution, however, be evaporated, crystals of a basic protonitrate having the composition $2HgO\ NO_5 + 2HO$ are formed. The only known method of obtaining crystalline neutral protonitrate from the preceding solution consists in immersing the latter in a freezing mixture. Both these nitrates are decomposed by dilution with water, the result being a white sub-nitrate, having the composition $3HgO\ NO_5 + HO$. Solution of protonitrate of mercury may be reduced to the condition of solution of nitrate of the suboxide $Hg_2O\ NO_5$ by boiling with more mercury.

Sulphate of Protoxide of Mercury.

This compound has already been cursorily mentioned. It is prepared, as we have seen, by boiling metallic mercury with strong sulphuric acid. The product should be heated in a sand-bath until copious fumes of sulphuric acid are evolved, and the material becomes dry, otherwise the result may probably be contaminated with a little sulphate of the suboxide. Sulphate of protoxide of mercury is an important material as constituting the basis of fabrication of both corrosive sublimate and calomel.

Subsulphate of Protoxide of Mercury (Turbeth's, or Turpeth's Mineral).

Many salts of mercury have the property, as we have seen, of suffering decomposition when water is added. Sulphate of protoxide of mercury is in this category, and the yellow powder thrown down is *subsulphate of protoxide.* Its composition is represented by the formula $3HgO.SO_3$.

Fulminate of Mercury, or Fulminating Mercury.

This salt is a compound of an acid, termed *fulminic,* with protoxide of mercury. Since the general adoption of the percussion principle in fire-arms, fulminate of mercury has become an important article of manufacture.

Preparation.—In general terms it may be said that fulminate of mercury is prepared by treating a solution of protonitrate of mercury with strong alcohol. Various details for manufacturing it exist; but the following proportions and directions answer well: dissolve 100 grains of mercury in a measured ounce of strong nitric acid, and, whilst yet hot, suddenly pour it upon a measured ounce and a half of alcohol, nearly absolute, contained in a flask or bottle of not less than three quarts capacity, and placed under a hood, or in the open air, but not exposed to the sun's rays. The action which ensues will be most violent, but not dangerous. Torrents of nitrous gases will be evolved, also some nitrous ether, and other complex products. When the action has ceased, and the bottle has become moderately cool, about a pint of cold distilled water is to be poured in, and the whole of the contents of the bottle, of which the fulminate of mercury is one, thrown upon a filter to be well washed. The safest method of retaining this dangerous compound is to keep it moist with water in a wooden or card-board box. Hard bodies should never be allowed to touch it, but portions, when wanted, should be scooped out by means of strips of paper or card.

Large quantities of the fulminate of mercury are made in the Channel Islands, on account of the low price of alcohol there. Mr. Taylor, the chief manufacturer of the substance in Guernsey, informs me that it is sent to England packed in canvas bags, surrounded with wet straw, in a hamper.

The compound wherewith percussion caps are filled is not pure fulminate of mercury, but an intimate mixture of that substance with about $\frac{4}{10}$ths of its weight of saltpetre. The two materials moistened with water are livigated together on a marble table with a wooden muller.

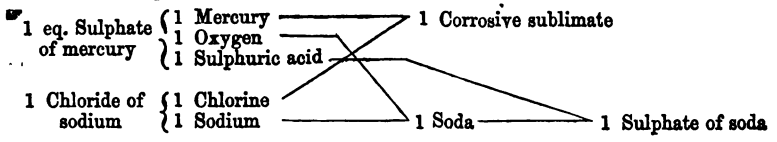
Chloride of Mercury (Corrosive Sublimate.)

This is an important mercurial preparation, not only as regards the numerous uses to which it is immediately applied in medicine and the arts, bnt as constituting the basis of preparation of the important medicinal substance calomel.

Preparation.—(1) By heating mercury in an atmosphere of chlorine.

(2) By dissolving oxide of mercury (red oxide) in hydrochloric acid and evaporating to crystallization.

(3) By subliming a mixture of equal parts of sulphate of mercury and common salt. This is the plan usually followed in practice, and the decomposition which ensues is thus represented :—



Properties.—A colourless crystalline body, having a specific gravity of 6·5. It fuses at about 509° Fah. Its vapour, which is colourless, has a specific gravity of about 9·42, referred to atmospheric air as unity. Corrosive sublimate requires about 16 parts of cold, and 3 parts of boiling water, for solution. Alcohol and ether both dissolve it in greater quantities, 3 parts of the latter, cold, dissolving one part of corrosive sublimate. The solubility of corrosive sublimate in ether is a very important quality, frequently taken advantage of in the extraction of that body from complex organic matters. Corrosive sublimate has the property of combining with albumen and some other organic matters, forming with them compounds nearly insoluble in water and in the usual contents of the stomach; hence albumen (white of egg), is an antidote to poisoning by this dangerous substance. A solution of protochloride of tin being poured into one of corrosive sublimate the latter is first converted into calomel; but on the addition of more protochloride of tin the calomel is itself decomposed, with production of metallic mercury, which precipitates in a finely divided state under the aspect of a black powder. Corrosive sublimate, although a more violent poison, weight for weight, than arsenious acid, is not so dangerous, for two reasons,—firstly, it possesses a strong metallic nauseous taste, unfitting it for the purposes of the murderer; secondly, its ill effects can be satisfactorily neutralized by the administration of white of egg beat up with water; a remedy, it will be remembered, already recommended in cases of poisoning by salts of copper.

Although albumen is pre-eminent amongst organic principles in the quality of combining with chloride of mercury and forming insoluble results, many organic matters are in the same category. On this fact depends the application of bichloride of mercury to the preservation of wood, cordage, &c. from decay. The organic combinations formed by it are not easily decomposed by ordinary atmospheric agencies, and are protected to some extent against fire. The preservative process of Kyan consists in steeping the wood, cordage, &c. in a solution of the chloride.

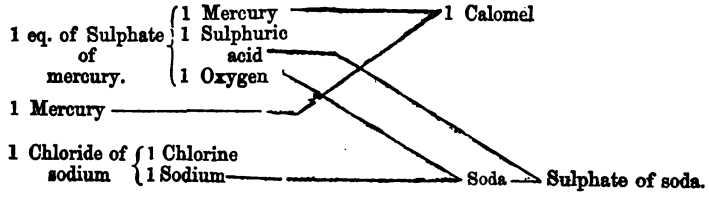
Preliminary qualitative test of the presence of Corrosive Sublimate in solutions both simple and complex.—A very elegant means of determining the presence of corrosive sublimate consists in placing a drop of the solution containing it upon a piece of gold, and touching both gold and solution with a piece of iron or steel. Practically the operation is usually conducted by means of a key and a gold coin. If corrosive sublimate or a few other salts of mercury be present, the metallic mercury will be deposited upon the gold, when the latter, on account of becoming amalgamated, will be marked with a white stain. *Practically*, the operator may take it for granted that an appearance of this kind will be produced alone by corrosive sublimate.

Separation of Corrosive Sublimate from organic mixtures.—The organic mixture should be placed in a flask having a long neck, and well agitated with ether; then being allowed to stand a short time at rest, the supernatant etherial layer should be removed, evaporated to dryness, the residue, if any, dissolved, and tested for corrosive sublimate. The tests will be indicated further on. It is impossible, by means of ether, to remove the whole of the corrosive sublimate which may be present in an organic mixture, hence the etherial treatment cannot become a means of *quantitative* separation. In cases of medico-legal examinations, however, involving corrosive sublimate, the problem is not usually to extract the *whole* of the poison, but to determine the presence of an amount sufficient to have destroyed human life. If the application of ether fail to result in the elimination of corrosive sublimate (which negative result may happen if very little of the poison be present), the operations become more abstruse, and will vary according to the kind of the organic matter present. For the processes necessary to be followed, I must refer to treatises specially written in this department of applied chemistry.

Sub- or Di-chloride of Mercury (Calomel).

Preparation.—(1) By mixing together solutions of sub-nitrate of mercury and of chloride of sodium (common salt).

(2) By triturating of corrosive sublimate with metallic mercury and common salt, subliming the mixture and condensing the result. This process is usually adopted in practice, and the decomposition which results is thus represented :—



Properties.—A heavy white crystalline body, though for medicinal uses it is generally obtained in powder. The specific gravity of calomel is 6·5; it is nearly insoluble in water. Solutions of alkalies, or alkaline earths, decompose calomel with production of black or suboxide (dinoxide) of mercury. Boiling nitric acid, or still more readily boiling nitro-hydrochloric acid, decomposes it, the former producing a mixture of nitrate of mercury and corrosive sublimate, the latter corrosive sublimate unmixed. When calomel is digested with solution of ammonia, a grayish-black powder falls, something like the suboxide of mercury in appearance, but which, however, is

probably a compound of that calomel with amidogen, and is, therefore, represented by the formula $Hg_2Cl.HgNH_2$.

White Precipitate.

Preparation.—By adding excess of ammonia to solution of corrosive sublimate a white powder (white precipitate) is thrown down. Its composition is still open to some doubt; but chemists, for the most part, adopt the opinion of Sir Robert Kane, that it is a compound of chloride of mercury (corrosive sublimate) with amidogen; in which case its composition will be represented by the formula $HgCl + HgNH_2$.

Combinations of Mercury with Iodine (Iodides of Mercury).

Two combinations of these elements are known; one corresponding with the sub, or black oxide, the other with the red, or protoxide of mercury.

Subiodide of Mercury.

Preparation.—(1) By adding solution of nitrate of suboxide of mercury to solution of iodide of potassium, a yellowish green powder is thrown down. It is the substance under consideration. (2) By triturating mercury and iodine together in the necessary atomic proportions—*i. e.* two equivalents of mercury and one of iodine. When heated rapidly, the subiodide rises in vapour unchanged; if slowly heated, however, it suffers decomposition into metallic mercury and the protoiodide of that metal.

Protoiodide of Mercury.

Preparation.—(1) By pouring solution of iodide of potassium into solution of corrosive sublimate, taking care that neither solution be in excess, the iodide of mercury being soluble in both.

(2) By triturating a mixture of metallic mercury and iodine in due atomic proportions.

Properties.—Protoiodide of mercury sublimes unchanged by heat, and its vapour is remarkable for its great specific gravity, 15·68; more considerable than that of any other known gaseous body. The salt under consideration furnishes a striking example of allotropism, evidenced as follows:—The protoiodide, when first obtained by precipitation, is a beautiful red compound; by application of heat, it first changes colour, the condition of powder being retained; it then, on the further application of heat, melts into a yellow liquid, and sublimes under the form of yellow crystalline spangles. Both the fused yellow mass and the yellow crystals resulting from sublimation retain their tint even after cooling; but if either be broken, the colour at once changes to red, first at the plane of rupture, but gradually extending to the whole mass; consequently, if the yellow iodide be *powdered*, the change takes place throughout the whole of the powder at once.

Cyanogen with Mercury (Cyanuret or Cyanide of Mercury).

Only one compound of mercury with cyanogen is known; it corresponds with corrosive sublimate, and is therefore the protocyanide, or protocyanuret of mercury. It is more usually called the bicyanide of mercury, however, owing to the opinion which formerly obtained, that the atomic weight now generally accepted for mercury should be doubled.

Preparation.—(1) By dissolving red oxide of mercury in dilute hydrocyanic acid, and evaporating the solution until crystals form.

(2). By boiling a mixture of two parts prussian blue, one part red oxide of mercury, and eight parts of water, filtering the solution, and setting aside to crystallize. If the filtered solution should contain traces of iron, which is frequently the case, that metal may be thrown down as oxide, by boiling the solution with a little red oxide of mercury.

(3) By boiling a mixture of two parts ferrocyanide of potassium (yellow prussiate of potash) with three of sulphate of mercury, and from fifteen to twenty parts of water. The liquor is to be filtered hot, and set aside to deposit crystals.

Cyanide of mercury is a white crystalline body, evolving cyanogen and metallic mercury when heated in a close vessel, and leaving a black residue termed paracyanogen. When hydrochloric acid is added to cyanide of mercury, and heat applied, mutual decomposition ensues, bichloride of mercury remaining behind, and hydrocyanic acid passing over. When cyanide and red oxide of mercury are boiled together union of the two results, and oxycyanide of mercury is formed. Cyanide of mercury also unites with other cyanides, forming, in many cases, well-defined crystalline combinations. It also unites with chlorides, iodides, and bromides, forming, in many cases, well-defined crystalline salts.

Combinations of Mercury with Sulphur.—Sulphurets, or Sulphides of Mercury.

Two of these compounds are known; one corresponding with the suboxide, the other with the red oxide of mercury.

Sub- or Di-sulphuret of Mercury.

If a stream of hydrosulphuric acid be transmitted through a cold solution of subnitrate of mercury, a black powder, which is the *sub-sulphuret of mercury*, falls. If the solution, however, be heated, the compound decomposes into metallic mercury and *protosulphuret*, the compound next to be described. A similar change also results when the sub-sulphuret is heated dry.

Sulphuret of Mercury.

Preparation.—(1) By triturating metallic mercury with sulphur in a mortar, sulphuret of mercury is obtained in the condition of black powder, formerly known by the appellation Ethiop's mineral.

(2) By transmitting a stream of hydrosulphuric acid gas through the solution of proto-salt of mercury. On first transmitting the current of gas, the precipitate which falls is white, being a compound of sulphuret of mercury with a definite portion of the mercurial salt originally present; at length, however, the current of gas being maintained, the precipitate which falls is black, being the true sulphuret of mercury.

Properties.—When the sulphuret of mercury, prepared as directed, is heated, it sublimes and condenses into a red mass, similar in appearance and identical in composition with the native sulphuret of mercury, called *cinnabar*. The red artificial sulphuret of mercury is called *vermilion*, and is much employed by painters. When designed for exclusive employment as a pigment, vermilion is prepared by a process different from that described. A very beautiful vermilion results when ordinary cinnabar, previously reduced to impalpable powder, is heated for a considerable period with solution of an alkaline sulphuret, at a temperature of about 112° Fah.

The sulphurets of mercury are readily decomposed when heated in the presence of atmospheric air, then sulphur being converted into sulphurous acid, and their mercury

sublimed. Cinnabar is readily attacked by hot nitro-hydrochloric acid, and with rather more difficulty by nitric acid; but hydrochloric acid and caustic alkalies dissolve it with difficulty.

General Characteristics of Mercurial Compounds.

Several mercurial compounds yield up their mercury by the simple application of heat, and all without exception are decomposed with the production of mercury when heated in contact with dry carbonate of soda. Most of the soluble compounds of mercury are decomposed, metallic mercury being thrown down by the combined voltaic action of gold and iron, as already indicated, also by a plate of metallic copper immersed in the solution. The greater number of mercurial solutions, if not all, are decomposed by protochloride of tin, metallic mercury being thrown down. The peculiar action of hydrosulphuric acid on soluble mercurial salts,—occasionally yielding a white precipitate, which, however, changes to black when more of the precipitant is added,—is important; also, the action of dry hydrochloric acid on di-solutions of mercury, causing the precipitation of an insoluble white powder (calomel). Iodide of potassium, too, is a delicate and characteristic test of mercury in solution, more especially for corrosive sublimate.

SILVER.

Equivalent or atomic weight . .	108·1
Specific gravity	10·5

Silver is a very widely distributed metal. It occurs as native or pure silver; also in combination with sulphur (sulphuret, or sulphide of silver), or with sulphur and lead, constituting the mineral galena, and in union with chlorine, forming chloride of silver.

Preparation of Silver Chemically Pure.—(1) 100 parts of chloride of silver are intimately mixed with 70 parts of carbonate of lime (chalk), and four or five of charcoal, and the mixture is heated to whiteness in an earthenware crucible. Carbonic oxide gas is liberated, and a mixture of chloride of calcium with metallic silver remains, the metal, however, forms a button, and collecting in the lowest part of the crucible is readily separated. Instead of the mixture of chalk and charcoal, carbonate of soda or of potash may be used.

(2) By suspending chloride of silver in water acidulated with a little hydrochloric acid, and immersing fragments of zinc. The chloride of silver by this treatment is rapidly decomposed, chloride of zinc being formed, and remaining in solution, and pure silver in a finely divided condition being thrown down. Practically, in order to assure the complete absence of zinc, it is as well to fuse the pulverulent silver resulting from this operation with a little nitric acid and borax. Instead of zinc iron may be employed; and this modification of the process is important as constituting the process by which silver is extracted from its ore, in America and in Saxony. The silver ore (a sulphuret) being reduced to powder is intimately mixed with common salt (chloride of sodium) and roasted in a furnace, by which treatment chloride of silver is generated, and the latter being intimately mixed with scraps of metallic iron and mercury, and well incorporated, an amalgam or compound of silver with mercury results. The latter is freed from a portion of its mercury by straining through a linen cloth, and finally the whole of the mercury is separated by distillation.

Characteristic Properties of Silver.

Silver absolutely pure is a soft metal yet harder than pure gold. On account of this softness it is neither adapted to the purposes of coinage, nor to the manufacture of articles of luxury. Pure silver, when polished, is more brilliant than any other metal, and does not tarnish by exposure to air either dry or moist, provided hydrosulphuric acid gas or vapours of hydrosulphate of ammonia be absent; otherwise it blackens. The black surface acquired by a silver spoon when immersed in mustard, or in a boiled egg, is also referable to a superficial combination with sulphur, and consequently demonstrates the existence of this element both in eggs and in mustard. Next to gold silver is the most ductile and malleable of all metals: it fuses at a white heat, and then absorbs oxygen, but the oxidation is not permanent, pure brilliant silver resulting as the metal cools. Silver is sparingly attacked by strong hydrochloric acid, even when hot; dilute sulphuric acid, too, exerts but little action upon it; strong sulphuric acid effects its solution, a portion of the acid being simultaneously decomposed, as evidenced by the disengagement of sulphurous acid gas. Nitric acid, whether dilute or concentrated, dissolves silver readily.

Combinations of Oxygen with Silver (Oxides of Silver).

Three compounds of oxygen with silver are known, namely, the suboxide Ag_2O; the protoxide AgO; and the binoxide AgO_2.

Sub-oxide of Silver.

Preparation.—By passing a stream of dry hydrogen gas over dry citrate of silver, heated to 212° Fah.

The citrate of silver, treated as described, loses oxygen, and assumes a brown tint. The product, when dissolved in water, yields a solution of citric acid, mixed with citrate of sub-oxide of silver. Solution of potash being acid, sub-oxide of silver precipitates. It is black, soluble in ammonia, and readily decomposed. When the mixed solution of citric acid and citrate of sub-oxide of silver is heated, citrate of protoxide of silver and metallic silver result, and the solution becomes colourless.

Protoxide of Silver.

Preparation.—When solution of potash is mixed in excess with a solution of nitrate of silver, black hydrated protoxide of silver falls. This compound loses its water of hydration when heated gently, or when subjected to the vacuum of an air-pump. Anhydrous protoxide of silver is an olive-coloured powder. Both hydrated and anhydrous protoxide of silver are decomposed by exposure to the sun's direct rays. The hydrated protoxide dissolves in water to a slight extent, and then manifests an alkaline re-action; but it is totally insoluble in caustic alkalies. All the *important* silver salts contain protoxide of that metal as base.

Binoxide or Peroxide of Silver.

Preparation.—When two platinum electrodes in action are plunged into a weak solution of nitrate of silver, the positive conductor soon becomes covered with black prismatic crystals of the binoxide or peroxide of silver. This compound is not so readily decomposed by heat as the protoxide, which is contrary to the general rule. It does not combine with acids, but decomposes, and yields salts of the protoxide.

Ammoniuretted Oxide of Silver.

This term may be provisionally applied to indicate a compound possessed of violently explosive qualities, and the composition of which is variously represented by different chemists. Some regard it as the result of a direct combination between ammonia and oxide of silver, having the formula $AgO + NH_3$; others believe it to be an amide of metallic silver, and consequently represented by the formula Ag, NH2; whilst, according to a third supposition, it is a direct compound of silver with nitrogen. This black fulminating oxide of silver must not be confounded with white *fulminate of oxide of silver*, formed by a process analogous to that adopted in the generation of fulminate of oxide of mercury. The black compound under consideration is as much more dangerous than the white fulminate of silver, as the latter in comparison with the corresponding salt of mercury.

Preparation.—The method of generating the black fulminating oxide of silver is here indicated, rather for the purpose of guarding the operator against the consequences of its accidental production than as a guide for its preparation. It may be formed by digesting oxide of silver with strong solution of ammonia; or by pouring solution of potash into a protosalt of silver dissolved in solution of ammonia. At a temperature of about 212° Fah. it explodes, even when covered by water, and mere friction with the plume of a feather causes detonation of the dry substance.

Salts of Protoxide of Silver.—Nitrate of Silver.

This very important salt has long been employed in medical and surgical practice, under the appellation of "*lunar caustic*," which substance is nitrate of silver fused, and cast into round sticks. The crystallized salt is now largely employed in calotype operations, and for many other purposes in the arts.

Preparation.—By dissolving silver in nitric acid moderately strong, and evaporating the solution until crystals form. If the silver employed be pure, the nitrate of silver resulting will be pure also; but in practice it is usual to employ, for the manufacture of this substance, silver which has been alloyed with copper, in which case one of the following modifications of the process just described has to be adopted:—(1) The whole of the alloyed silver having been dissolved, the solution is evaporated to dryness and the dry mass fused. By this treatment the nitrate of copper is decomposed into the elements of nitric acid, which being volatile are evolved, and oxide of copper, which remains diffused through the liquified nitrate of silver, which is coloured brown in consequence. From time to time a little of the fused product is removed on the extremity of a glass rod, dissolved with water, and tested by ammonia; so long as any nitrate of copper remains undecomposed, the solution turns blue when ammonia is added; but as soon as the decomposition of nitrate of copper is complete, this change does not take place. The fused mass being now removed from the fire, allowed to grow cold, dissolved in water, and the solution filtered, yields a solution of pure nitrate of silver, which is to be evaporated as before until crystals are produced. (2) A solution of mixed nitrate of silver and nitrate of copper having been made, one-fifth part of it is to be precipitated by cold potash solution added in excess. By this treatment all the oxide of silver and oxide of copper is thrown down. The mixed oxides having been well washed for the puspose of removing potash, are to be added to the remaining four-fifths of the solution and boiled, by which treatment the whole of the oxide of copper

is thrown down, and a solution of pure nitrate of silver remains, which is to be treated as before.

Nitrate of silver, when quite free from all organic matter, does not perceptibly decompose when subjected to the sun's direct rays; but the slightest admixture of organic matter leads to that result.

Sulphate of Silver.

Preparation.—(1) By digesting silver with concentrated sulphuric acid.

(2) By adding sulphuric acid or sulphate of soda to a boiling solution of nitrate of silver.

Properties.—A white crystalline body, though the crystals are usually small, soluble in water to a slight extent only, but more soluble in solution of ammonia.

Carbonate of Silver.

Preparation.—By adding carbonate of soda to a solution of nitrate of silver.

Properties.—A white powder, which changes to brown by exposure to the sun's rays, and suffers decomposition when heated, either dry or surrounded by water, metallic silver in both cases being the fixed result of decomposition.

Acetate of Silver.

Preparation.—By dissolving carbonate of silver in acetic acid, or by pouring solution of acetate of soda into a hot and concentrated solution of nitrate of silver.

Hyposulphite of Silver.

This salt is a white powder which suffers decomposition when boiled with water, metallic silver being precipitated. Hyposulphite of silver readily combines with alkaline hyposulphites, generating solutions characterized by an intensely sweet taste. Alkaline hyposulphites, moreover, dissolve chloride and oxide of silver, yielding solutions somewhat brown in appearance, and also sweet. This property of the alkaline hyposulphites renders them applicable to the calotype operation as solvents for certain argentiferous depositions, which, if allowed to remain, would be injurious to the picture.

Combinations of Silver and Sulphur.—Sulphurets or Sulphides of Silver.

Only one compound of sulphur with silver, the *monosulphuret* or *monosulphide* is known. It occurs native, crystallizing in forms isomorphous with those of the subsulphuret of copper. Sometimes it is found pure, but more generally in combination with sulphurets of arsenic and antimony. Sulphuret of silver of the same chemical composition may also be formed by fusing silver and sulphur together in single atomic proportions, or by precipitating solution of a silver salt by hydrosulphuric acid or hydrosulphate of ammonia.

Silver with Chlorine—Chloride of Silver.

Only one chloride of silver is known; it is the protochloride, and a very important compound. Chloride of silver is occasionally found native, and may be prepared by adding hydrochloric acid, chlorine, or any soluble chloride, to solution of nitrate of

silver, or *almost* any argentiferous solution. It is a dense flocculent white powder, the particles of which cohere by agitation, and form acid masses, which are highly characteristic. The precipitate separates most satisfactorily from solutions acidulated by nitric acid, and heated. Chloride of silver is not soluble in water to an appreciable extent, but slightly soluble in hot concentrated hydrochloric acid. Ammonia solution dissolves it with facility, and serves to distinguish it from subchloride of mercury (calomel), which it closely resembles in physical appearance. Calomel is blackened by the addition of solution of ammonia, whereas chloride of silver, as we have seen, is dissolved by that reagent.

Chloride of silver is blackened by exposure to the sun's rays, possibly owing to conversion into subchloride, but the rationale of the change is not fully understood. The blackened portion is no longer dissolved either by ammonia or alkaline hyposulphites, whereas the white portion is dissolved in both. Chloride of silver fuses at about 500° Fah., and, on cooling, forms a semi-transparent horny mass; at a still higher temperature it may be partially volatilized. The methods of effecting its decomposition, and producing its metallic silver, have already been adverted to at page 501.

Silver with Iodine, and with Bromine.

The iodide of silver is a yellowish white powder, thrown down when solution of an iodide is added to solution of a silver salt. Nitric acid and ammonia dissolve it to a slight extent, whereas chloride of silver is readily soluble in ammonia, as we have seen, as in like manner is bromide of silver. The latter salt is prepared like the iodide merely employing a soluble bromide in place of a soluble iodide.

Silver with Cyanogen.

When hydrocyanic acid is poured into a solution of nitrate of silver, a curdy white precipitate, *cyanide of silver falls.* By this means the quantity of hydrocyanic acid present in a solution may be determined. Cyanide of silver is not soluble in water, nor in dilute and cold nitric acid; but solution of ammonia dissolves it with facility. Treated with hydrochloric acid, decomposition ensues, chloride of silver and hydrocyanic acid being simultaneously generated. Occasionally the dècomposition is taken advantage of in effecting the extemporaneous preparation of hydrocyanic acid.

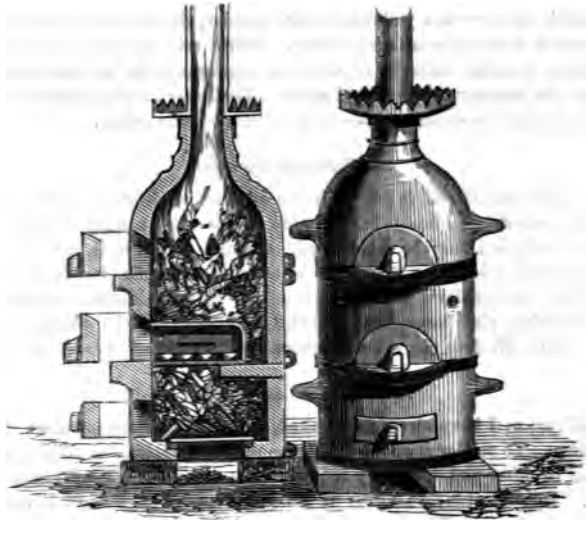
Silver Assaying.

Pure silver, as I have already remarked, is too soft for the purposes of coinage and manufacture. To render it adapted to these uses it is melted, or *alloyed*, with a certain per centage of other metal, usually copper. The amount of alloy varies for different countries. English standard silver is composed of 11 oz. 2 dwts. silver melted with 18 dwts. pure copper. The per centage composition of a silver alloy can, of course, be ascertained by one of several processes of chemical analysis. Practically, however, the operations are reduced to two; the dry and the moist processes of silver assaying. In England, the former is almost exclusively employed, though in France the latter is followed by preference. The dry process of silver or gold assaying involves the operation of *cupellation*, as it is termed, the outline of which I shall now proceed to describe.

Cupellation.—Pure silver may be fused without any permanent oxidation, and a similar remark applies to gold and platinum. The latter metal may be left out of

consideration; hence, practically the only metals we have to consider as the objects of cupellation are silver and gold. Excluding platinum, then, all other metals, except silver and gold, are converted into oxides when kept fused for a considerable time. Lead is pre-eminent in this respect; not only does it oxidise with extreme facility, but the oxide, when generated, readily fuses, and acts as a solvent for other oxides, especially that of copper. If, then, the fused oxides could be successively removed, as soon as formed, the silver contained in an alloy free from gold would eventually remain pure. On a proper application of these principles depend the process of cupellation, so called from the employment of a little cup, or crucible, technically denominated *a cupel*, made of bone earth, a material which is endowed with the quality of absorbing the fused oxides after the manner of a sponge.

The operation is conducted in the following manner:—A weighed portion of silver alloy, usually not more than 12 grains, being wrapped in sheet lead, absolutely pure, is thrown upon a cupel heated to redness in a small oven, through which a current of atmospheric air continually passes. This oven is technically known as a muffle, and the manner of fixing it in the assaying furnace is represented by the following engravings:—



The process of cupellation does not give results absolutely correct, especially if the heat employed be unnecessarily high, inasmuch as silver is perceptibly volatile under these circumstances; but, on the other hand, a portion of the lead employed remains obstinately combined with the silver, and thus in some measure compensates for the proportion of that metal lost by evaporation. Usually the cupelling process occupies about twenty minutes, and may be known to have been continued sufficiently long by a peculiar appearance, termed "brightening."

assumed by the silver bead. Whilst any lead or other base metal remains to be removed, the bead of impure silver is seen to emit fumes, to be tinted with iridescent colours, and to be violently agitated; suddenly, however, a flash of light appears, the iridescence and motion cease, the bead becomes dead white and motionless. The operator must now draw the cupel towards the external orifice, or mouth of the muffle, and there allow it to remain until it becomes partially cold, when it is to be withdrawn completely, allowed to become quite cold, and weighed. The loss of weight is indicative of the per centage of base metal originally present. If the cupel with its contents be withdrawn abruptly, the bead of silver is liable to shoot forth fungoid-looking excrescences, occasionally with such violence that particles of silver are darted away, and lost. This phenomenon is dependent on the fact, that pure silver, when fused, absorbs a considerable amount of oxygen, which does not contribute to form a permanent oxide, however, but is evolved as the silver cools.

The moist process of silver assaying is founded upon the fact that all the silver contained in an alloy may be precipitated from solution by means of a soluble chloride. Chloride of sodium (common salt) is the material employed for this purpose, and the estimation is made in France volumetrically; that is to say, the solution of common salt is determinate, in such manner that a given volume used corresponds with a known portion of silver. If time be not an object, the estimation of silver as chloride may be effected by weighing instead of measuring the quantity of solution used; in which case the test solution should be poured into the argentiferous solution from a Schuster's alkalimeter—the instrument represented at p. 413.

GOLD.

Equivalent or atomic weight . . .	197
Specific gravity	19·5

Gold is almost invariably found in the metallic state—not, however, pure, being contaminated usually with silver or copper, or both, and more rarely with tellurium, and with palladium. Gold is but rarely obtained from mines; in the form of nuggets or metallic lumps, it is collected by manual labour, and when the particles are too small for this treatment they are usually extracted either by means of mercury (amalgamation) or more rarely by the agency of chlorine.

Gold, though a scarce metal, is very widely diffused. There are but few parts of the world in which gold has not been found to some extent, but California and Australia have yielded it in larger quantities than any other regions. Gold, like silver, is too soft for adaptation to the purpose of coinage or ornamentation; hence it must be alloyed, and the base metal added is usually copper, though occasionally other metals such as silver and zinc are used. The student may have remarked that English sovereigns and half sovereigns coined before the year 1826, are lighter in colour than those subsequently produced; which is referable to the fact of their holding in their composition a portion of silver. The per centage of alloy metal is fixed by law in all civilized countries, and differs according to the use to which the gold is intended to be applied. English gold coins are made of twenty-two parts pure, or fine gold, alloyed with two parts copper; in other words, one part copper to eleven of gold—the reason why two parts to twenty-two, instead of one to eleven, will be explained presently. The legal ratio of admixture adopted in France for the gold pieces of that nation is one to nine.

Combinations of Gold with Oxygen.

Gold may be fused and exposed to contact with atmospheric air for an indefinite period, without the generation of an oxide; nevertheless, by chemical treatment two distinct oxides of gold may be generated, the sub-oxide Au_2O and the sesquioxide or peroxide Au_2O_3.

Sub-oxide of Gold—(Au_2O).

Preparation.—When potash solution is added to solution of sub-chloride (dichloride of gold) a powder of deep violet colour, which is the oxide in question, falls. Oxyacids have no action upon it, but hydracids decompose it, sesquichloride of gold Au_2Cl_3 being formed and metallic gold deposited.

Sesquioxide or peroxide of Gold, also called Auric Acid.

Preparation.—By digesting a solution of perchloride of gold with magnesia, aurate of magnesia mixed with free magnesia is obtained. When this mixture is boiled with nitric acid the magnesia dissolves, and hydrated sesquioxide of gold remains. It is a yellowish-red powder when hydrated, turning to chesnut-brown when dried. Heat and direct solar light effect its decomposition into oxygen, and metallic gold; when boiled with deoxidising agents, such as alcohol or sulphurous acid, also many of the organic acids, the same result occurs. Neither this nor the preceding oxide forms definite compounds with acids.

Ammoniacal Oxide of Gold or Fulminating Gold.

When solution of ammonia is poured into sesquichloride of gold, a precipitate possessing fulminating properties deposits. Its composition has not been quantitatively determined, but it is known to contain oxide of gold, ammonia, and chlorine. If this compound be digested in a further quantity of ammonia, a brown powder remains which is fulminating gold, properly so called. According to the opinion of most chemists it is a combination of sesquioxide of gold with ammonia.

Gold with Chlorine—Chlorides of Gold.

There are two combinations of gold with chlorine, corresponding with the two oxides of gold. The sesquichloride is the product of dissolving gold in nitrohydrochloric acid (aqua regia). By evaporating the solution to dryness, a yellow crystalline material composed of hydrochloric acid and sesquichloride of gold results; and this, when still more heated, suffers partial decomposition, hydrochloric acid being evolved and sesquichloride of gold remaining. It is a brown deliquescent material, very soluble in alcohol and ether; the latter of which even removes sesquichloride of gold from its aqueous solution.

Subchloride, or Dichloride, of Gold.

When the preceding compound is exposed to a temperature not exceeding 440° Fah., chlorine is evolved and dichloride of gold remains. It is yellowish, non-crystalline, and insoluble in water.

Gold with Sulphur—Sulphurets or Sulphides of Gold.

Two of these compounds are known, corresponding with the oxides, and the chlorides of gold respectively. They are formed by transmitting hydrosulphuric acid through solutions of sesquichloride of gold. If the solutions be hot, the dark-brown di-sulphuret is precipitated; but if cold, the black powder which falls is the sesquisulphuret of gold.

Gold Assaying.

The operation of gold aasaying involves the two processes of cupellation, already described, and quartation. If, instead of a compound of silver with oxidisable metal, a compound of gold, and the same be cupelled with lead a bead of pure gold will remain; if, however, a compound of gold, silver, and base, or oxidisable metal be cupelled, the result of cupellation will be an alloy of pure gold and pure silver combined.

Now gold is not soluble in nitric acid, whereas silver readily dissolves in that menstruum; hence theory suggests that all the silver contained in an argento-auriferous alloy should be capable of removal by the action of hot nitric acid, leaving the gold behind. Practically, however, this result does not ensue except the silver present amount to not less than two-thirds of the total weight of the mixed metals. Hence the process of gold assaying resolves itself into the following general scheme: the assayer having formed a judgment, from the colour and general appearance of the alloy, as to the amount of silver present, adds such a known excess of pure silver as when fused with the gold shall yield a button having the composition of about three parts, by weight, of silver to one of gold. The compound is now wrapped in thin sheet lead and cupelled in the ordinary manner; the result of which operation is a button of gold mixed with silver. This product is next flattened into a plate or ribbon, heated to render it soft, converted into a flat helix termed a cornet, by winding it round a quill or other small cylinder, and boiled with nitric acid. By this treatment the whole of the silver is dissolved, and the gold remains. When first withdrawn from the nitric acid the gold helix is friable and devoid of the metallic appearance; after being heated, however, its particles cohere, and its surface assumes the golden aspect. It has already been stated that although the proportion of alloy in English gold coins is one to eleven, the proportion is invariably expressed as two parts to twenty-two. The origin of this custom is as follows: every portion of gold, whether large or small, is assumed to be divided into twenty-four equal parts, termed *carats*, and the actual quantity of pure gold present is spoken of as so many carats fine. For example—absolutely pure gold, or that which is devoid of all mixture of base metals, is said to be twenty-four carats fine, or two carats better than standard, whereas gold containing four parts of base metal in the twenty-four, is said to be gold of twenty carats fine, or two carats worse than standard, &c.

General Characteristics of Auriferous Solutions.—Solution of gold in nitrohydrochloric acid is the only one which usually occurs. The presence of gold in it may be detected by the following characteristics:—

(1) Solution of protochloride of tin throws down a precipitate, the exact composition of which is still undetermined, but which is known as the "*purple powder of Cassius.*" The purple colour is scarcely evident in the powder itself, but becomes manifest when the latter is fused with borax.

(2) Solutions of protosalts of iron, when heated with the auriferous solution, throw down metallic gold.

(3) A current of hydrosulphuric acid, solution of that acid in water, or hydrosulphate of ammonia, throws down a brown or black precipitate, which, on the application of sufficient heat, decomposes, evolves the elements of hydrosulphuric acid, and leaves a fixed residue of metallic gold.

PLATINUM.

Equivalent, or atomic weight .	98·7
Specific gravity . . .	21·5

This metal was only introduced into Europe towards the middle of the last century; though, under the name of *Platina*, diminutive of *Plata*, and signifying little silver, it had long been known to the American Spaniards. Platinum is the most infusible of metals, and the heaviest of all known bodies. It cannot be melted in the strongest heat of furnaces, but it fuses before the hydro-oxygen flame, or when held in the luminous arc which extends between a pair of voltaic charcoal electrodes in powerful action. Besides this quality of difficult fusibility, platinum is not attacked by the strongest acids; hence it becomes important to the chemist, as a material for many of his instruments.

Preparation of absolutely pure Platinum.—Platinum of commerce is nearly pure, only containing a minute portion of iridium, which increases the hardness of platinum, but lessens its malleability. To obtain platinum absolutely pure, the scheme of operation is as follows:—A solution of commercial platinum is effected in nitrohydrochloric acid (chloride of platinum), and solution of chloride of potassium is added. The yellow precipitate which deposits is a mixture of the double chloride of potassium and platinum, with the double chloride of potassium and iridium. The precipitate having been intimately mixed with carbonate of potash, is heated to redness in a crucible of porcelain. The result of this operation is metallic platinum and oxide of iridium, mixed with chloride of potassium. The alkaline residue having been dissolved out by hot water, the mixture of oxide of iridium and metallic platinum is treated with dilute nitrohydrochloric acid, which only dissolves the platinum. Sal-ammoniac being now poured into the platinum solution, the double chloride of platinum and sal-ammoniac ($PtCl_2 + NH_3 HCl$) falls, and on the application of sufficient heat is decomposed; metallic platinum, in minute state of division (spongy platinum), being the sole residue.

Inasmuch as platinum, like iron, admits of being welded, the spongy platinum just described if heated to complete whiteness and strongly compressed in a mould, admits of being brought to the condition of *bar-platinum*; and this latter, by rolling, may be converted into platinum sheet. This, indeed, is an outline of the processes followed on the large scale of platinum manufacture.

Properties.—The three most prominent characteristics of platinum are its extreme density, its difficult fusibility, and its resistance to the solvent power of acids. Hydrochloric and sulphuric acids, whether hot or cold, are completely devoid of action on platinum; nor does nitric acid dissolve it under ordinary conditions. Nevertheless, if platinum be alloyed with silver to a sufficient extent, and the alloy be acted upon by nitric acid, both platinum and silver are taken up. The best solvent

for platinum is chlorine; nitrohydrochloric acid being the chloriniferous fluid usually employed for this purpose.

Though platinum resists the action of acids, and therefore has an extensive sphere of application in chemical operations, nevertheless it is a treacherous metal, and vessels made of it are soon injured, if the substances capable of uniting with it are not borne in mind. Vessels of platinum cannot be employed for effecting the fusion of other metals; they are spoiled by heating in contact with sulphur, or any compound which readily evolves sulphur: phosphorus and arsenic, too, damage them, and also caustic alkalies, and mixtures of caustic alkalies with nitrates of the same. Platinum crucibles, moreover, are injured by the prolonged contact of incandescent charcoal; an effect which is due, apparently, to the action of silicic acid contained in the charcoal. Platinum crucibles are generally heated *naked* over the flame of gas, or of a spirit-lamp, or in a small furnace containing charcoal; but if the operation of heating is required to be of long duration, the platinum crucible should be protected, by bedding it in an earthenware crucible, having magnesia tightly impacted between the two.

Platinum, when obtained in a very fine state of mechanical division, is endowed with some curious properties. One form of finely-divided platinum (spongy platinum) has already been described; the substance termed *platinum black* furnishes the metal in a condition of still more minute division. Platinum black may be prepared by three processes.

(1) By boiling solution of chloride of platinum, $PtCl_2$, with carbonate of soda and sugar, collecting the precipitate, washing and drying.

(2) By dissolving protochloride of platinum ($PtCl$) in a solution of potash, boiling, and adding alcohol until a precipitate no longer forms, washing and drying.

(3) By the addition of alcohol to solution of sulphate of platinum.

The metal in all these states of fine division has the property of absorbing oxygen, and producing some curious phenomena of combustion. This peculiarity is taken advantage of in several chemical operations. For example, a mixture of chloroplatinate of ammonia, sal-ammoniac, and clay, when made in the form of pellets and strongly ignited, yields a porous mass of clay and finely-divided platinum, much employed by chemists for effecting the combination of hydrogen and oxygen gases, in certain cases where the electric spark would be inapplicable. A pellet of this kind is also sometimes employed as a means of instantaneous light, by directing upon it a jet of hydrogen, which, if the pellet be in good working order, soon inflames. These combustive effects are still more conspicuously displayed by platinum black, especially the variety made from sulphate of platinum, and are sometimes employed for technological purposes. Thus, if a small stream or continuous drops of alcohol be permitted to fall upon platinum black, the latter soon begins to glow, and the alcohol is decomposed, the chief result of decomposition being acetic acid. In this manner acetic acid is sometimes prepared in Germany.

Although finely divided platinum, as we have it in platinum sponge or platinum black, manifests the combustive phenomena just adverted to in an extreme degree, yet platinum in mass manifests a similar tendency, as may be illustrated by the very common experiment of surrounding the wick of a spirit lamp with fine platinum wire, igniting the wick until the wire is incandescent, then blowing out the flame. Under these circumstances slow combustion of the alcohol ensues, and the platinum wire remains incandescent.

Platinum with Oxygen—Oxide of Platinum.

Platinum is known to unite with oxygen in two proportions, producing respectively protoxide and binoxide, or peroxide of platinum, having the respective compositions of PtO and $Pt\,O_2$.

Protoxide of Platinum.

Preparation.—By the addition of caustic potash to solution of protochloride of platinum, the precipitation of a black powder, hydrate of protoxide of platinum is effected. It dissolves in both alkalies and acids.

Binoxide of Platinum.

Preparation.—By adding a considerable excess of caustic potash to solution of perchloride of platinum, boiling the yellow precipitate in its fluid of precipitation, and adding acetic acid to the boiled liquor. The powder which forms is hydrate of peroxide of platinum. When heated it evolves water and becomes anhydrous. The hydrated oxide dissolves in acids and in caustic alkalies, but the anhydrous oxide does not.

Salts of the Oxides of Platinum.

Both protoxide and binoxide of platinum when hydrated can be made to unite with acids. The salts of the former are unimportant. Only one, the oxalate, has hitherto been obtained in the crystalline state. Caustic potash yields no precipitate with dilute solutions of these salts; alkaline carbonates throw down a brown precipitate, and hydrosulphuric acid and the alkaline hydrosulphates a black precipitate.

Salts having binoxide of platinum as their basic constituents are all yellow or orange. Caustic potash precipitates from their solutions the brown platinate of potash. Hydrosulphuric acid and alkaline hydrosulphates throw down a black precipitate, and zinc and iron both cause the deposition of metallic platinum in the condition of black powder. With chloride of potassium, and with sal-ammoniac (chloride of ammonium), salts of binoxide of platinum yield yellow precipitates, the double chlorides respectively of chloride of potassium with chloride of platinum ($Pt\,Cl_2 + KCl$), and hydrochlorate of ammonia, or chloride of ammonium, with chloride of platinum ($Pt\,Cl_2 + NH_3H\,Cl$).

Both these double chlorides are decomposed by heat, the ammonia compound yielding platinum in the condition of a spongy mass (spongy platinum), and the potassium compound a mixture of metallic platinum and chloride of potassium. Chloride of sodium yields no precipitate; hence a soluble salt of binoxide of platinum, or what in practice is more convenient, solution of bichloride of platinum, is used not only to distinguish between potash ammonia and soda, but occasionally to separate the two former, and determine their proportions. Now, inasmuch as ammonia is composed of NH_3, it follows that the chloroplatinate of ammonia, as the double chloride of platinum and ammonium is termed, may be made the basis of ascertaining the amount of nitrogen contained in any body, provided that nitrogen exist in the form of ammonia. One of the processes of determining the amount of nitrogen contained in organic bodies (the process of Varrentrapp and Will) is founded on this principle. The organic nitrogenous body being ignited in contact with soda and lime, all the

nitrogen becomes converted into ammonia, which being transmitted through a solution of hydrochloric acid is absorbed; and the solution being precipitated by chloride of platinum, is collected, dried, weighed, and the amount of nitrogen present determined by an obvious calculation. Both the chloroplatinate of potassium and of ammonium are nearly insoluble in cold water; but alcohol, and still better a mixture of alcohol and ether, added to the liquor of precipitation, renders the precipitate still more insoluble.

Sulphate of Binoxide of Platinum.

This salt is interesting as furnishing the best source from which to obtain platinum black. It is made by digesting sulphuret of platinum (formed by passing hydrosulphuric acid gas through solution of chloride of platinum) with sulphuric acid.

Chlorides of Platinum.

These salts are far more important than any of the platinum salts which have been adverted to. There are two chlorides of platinum, the protochloride and the bichloride, corresponding respectively to the two oxides. It will be convenient to describe the bichloride of platinum first.

Bichloride of Platinum.

Preparation.—When platinum is dissolved in nitro-hydrochloric acid, solution of bichloride of platinum is obtained, mixed, however, with some nitric and hydrochloric acids. These, however, may be dissipated by cautious heating, when the bichloride of platinum remains pure. It dissolves in water, furnishing a yellow solution. This chloride does not crystallize.

Protochloride of Platinum

is obtained from the bichloride by exposing the latter to a heat not exceeding 390° Fah. It is a greenish powder, insoluble in water, soluble in hydrochloric acid, and yields no precipitate with either hydrochlorate of ammonia or chloride of potassium.

OSMIUM.

Equivalent or atomic weight	19·6
Specific gravity	(about) 10

Preparation.—By heating the double chloride of osmium and ammonium.

Properties.—A white metal, not quite devoid of malleability, but nevertheless brittle; exceedingly infusible. When heated, it rapidly combines with oxygen, becoming osmic acid. Nitric acid dissolves it, generating osmic acid. Nitrohydrochloric acid effects this change with still greater facility. When osmium is sharply heated in contact with caustic alkalies, and alkaline nitrates, alkaline osmiates are formed. Finely-divided osmium, when heated in the air, oxidizes, with formation of osmic acid, characterized by a very peculiar smell, indicative of the presence of osmium, the name of which,—from *'οσμή*, smell,—was suggested by the odoriferous quality of osmic acid.

Compounds of Osmium with Oxygen—Oxides of Osmium.

Five of these compounds are known, and their composition is thus represented:—

Protoxide	$OS\ O$
Sesquioxide	$OS_2\ O_3$
Binoxide	$OS\ O_2$
Osmious acid	$OS\ O_3$
Osmic acid	$OS\ O_4$

Protoxide of Osmium.

Preparation.—When potash solution is added to the double chloride of osmium and potassium, a dark green powder precipitates. It is the protoxide of osmium, which dissolves in acids, forming green solutions.

Sesquioxide of Osmium.

Preparation.—When a mixture of osmic acid with ammonia is heated for a considerable period at a temperature of about 112° Fah., sesquioxide of osmium, mingled with ammonia, from which it cannot be separated, is obtained. This oxide dissolves in acids, and yields non-crystallizable yellow solutions.

Binoxide of Osmium.

Preparation.—By transmitting chlorine through a mixture of finely-divided osmium and chloride of potassium, a double chloride of osmium and potassium, having the formula $Os\,Cl_2 + KCl$, is obtained. When to this salt a cold solution of carbonate of potash is added, a black powder, which is binoxide of osmium, results.

Osmic Acid.

The formation of this compound, by strongly heating metallic osmium in presence of atmospheric air, has been already noticed. The change takes place still more satisfactorily if oxygen gas be substituted for atmospheric air. It is also generated when osmium is digested with nitric or nitro-hydrochloric acid, or strongly heated with nitrate of potash; and, lastly, when an osmiate is decomposed by a stronger acid.

Osmious acid has never been isolated. Osmite of potash may be obtained by mixing a little alcohol with solution of osmiate of potash.

The preceding general indications of the chemical bearings of osmium will render the method of obtaining this metal from its ore intelligible. Osmium almost invariably accompanies native platinum. It is found united with iridium, another metal to be presently described, forming scales, or occasionally crystals of the substance termed *osmiuret of iridium.* This compound not being easily soluble in *aqua regia* remains behind when native platinum is subjected to that menstruum. Osmium may be obtained from the osmiuret of iridium by a process of which the following is an outline:—100 parts of powdered osmiuret of iridium are intimately incorporated with 300 parts of nitre, and heated to redness. The fused mass which contains osmiate

and iridiate of potash being poured upon a flat surface, is broken small, introduced into a glass retort, and an excess of nitric acid added. A cooled receiver being adapted to the retort, and heat applied, osmic acid distils over, and deposits in the form of white crystals. These being dissolved in solution of potash, and alcohol added, osmite of potash falls, from which osmium and its compounds may be prepared by processes which are obvious.

The matter remaining in the retort after all the osmic acid formed has come over is chiefly oxide of iridium, mixed, however, with some oxide of osmium. The mixture being dissolved in *aqua regia*, and hydrochlorate of ammonia added, both the iridium and the osmium are precipitated in the form of ammoniacal chlorides, the composition of which, if the symbol M stand for *metal*, may be represented by the general formula $MCl_2 + NH_3HC$. If these mixed ammoniacal chlorides be suspended in water, and a current of sulphurous acid transmitted, the insoluble ammoniacal chloride of iridium $IrCl_2 + NH_3$ is changed into the soluble ammoniacal chloride $Ir.Cl + NH_3HCl$, whilst the ammoniacal chloride of osmium remains unchanged. When strongly heated it yields metallic osmium.

IRIDIUM.

Equivalent, or atomic weight	99
Specific gravity	?

Preparation.—The soluble ammoniacal chloride of iridium, described in the last paragraph, deposits in crystals when the solution containing it is evaporated. When these crystals are strongly heated they yield metallic iridium in the condition of powder. Iridium is still less fusible than platinum; but if the powder be heated to whiteness, and strongly pressed, it aggregates into a mass, still not devoid of porosity, but exceedingly hard. Pure iridium neither dissolves in nitric acid nor in *aqua regia*, but it dissolves in these when alloyed with other metals.

Iridium yields four oxides, four chlorides, and one sulphuret.

PALLADIUM.

Equivalent or atomic weight	53·3
Specific gravity	11·8

This metal is also obtained from platiniferous minerals and from a certain Brazilian gold ore; in appearance it is intermediate between platinum and silver. It is considerably more fusible than platinum, and, like platinum, soft, malleable, ductile, and capable of being welded when heated to whiteness. Palladium is applied to many useful purposes. Dentists sometimes employ it to form artificial palates; opticians use it occasionally in the formation of graduated scales; and the manufacturers of weighing-balances for the beams of these delicate instruments. For all these purposes the metal palladium is well adapted, not being acted on by any ordinary atmospheric impurity.

Combinations of Palladium with Oxygen.

There are two oxides of palladium,—the protoxide and the binoxide; the latter, however, has never been isolated,

Combinations of Palladium with Chlorine.

Nitric acid can dissolve palladium; but chlorine is a better agent. *Aqua regia* is

the chloriniferous menstruum generally employed. There exist two chlorides of palladium corresponding in general relations to the two chlorides of platinum.

Cyanogen with Palladium—Cyanide of Palladium.

Cyanogen and palladium have a great affinity; so that when a soluble cyanide, such as cyanide of mercury or of potash, for example, is poured into a neutral solution containing palladium, the metal separates as cyanide. It is by taking advantage of this property of cyanogen to unite with palladium that the metal is separated from its associates,—platinum and gold.

RHODIUM AND RUTHENIUM.

These metals are also found associated with platinum, and the former occasionally with gold. Rhodium is obtained from the mother liquid, out of which platinum and palladium have both been separated. It is obtained by taking advantage of the insolubility of the double chloride of rhodium and sodium in alcohol. Rhodium is so called on account of the rose-colour of its solutions. It is a very hard white metal, even more infusible than platinum. It forms two oxides, two chlorides, and a sulphuret. Ruthenium very much resembles iridium, with which it was for a long time confounded.

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